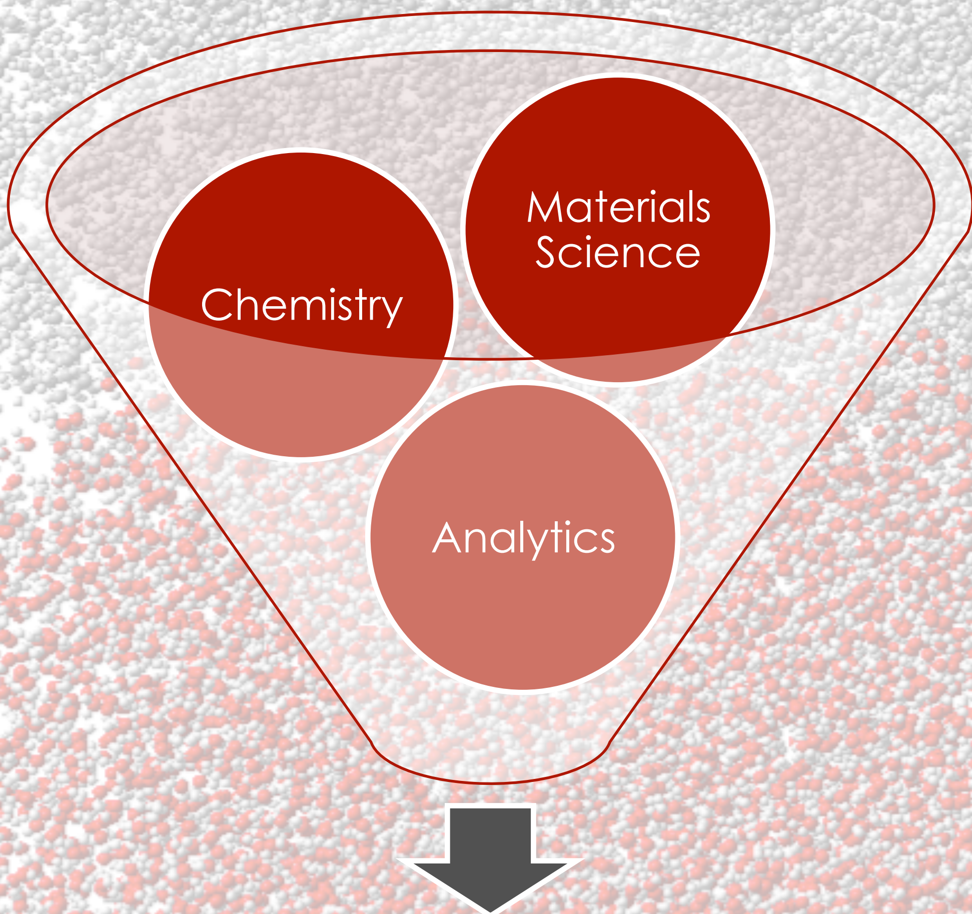
Realistic Multiphase Simulations for Separations of Multicomponent Actinide Bearing Waste

Aurora Clark
Department of Chemistry
Materials Science and Engineering Program
Washington State University

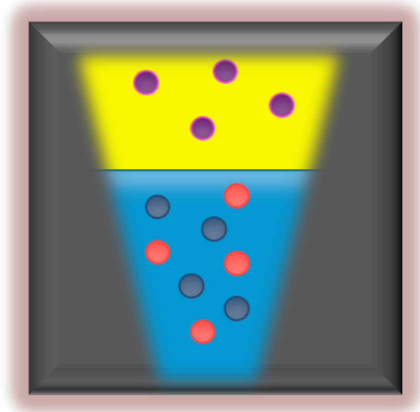
Computational Research in the A. Clark Research Group



Predictive Science and New Theories for Liquids and Their Interfaces

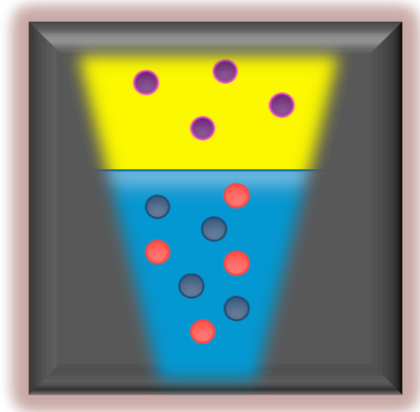
Separations
Synthesis
Multicomponent non-ideal solutions

Introduction to Solvent Extraction



- Major industrial process for separating complex mixtures in:
  - Organics:
    - Biomass production into chemical commodities (organics)
  - Inorganics:
    - Mining industry (ore → specific metal of interest)
    - Chemical industry (catalysis)
    - Environmental cleanup at hazardous waste sites (heavy metals)
    - Metal recycling
    - **Energy industry: Nuclear Energy and Next Generation NE**

Working Conditions in Extraction



Organic Phase

-single to multicomponent

-solutes acting as modifiers

Aqueous Phase

-High ionic Strength

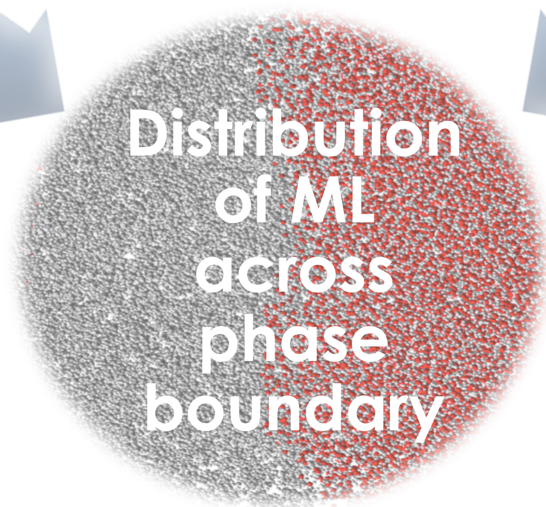
-High acidity

-Complex mixture of metals

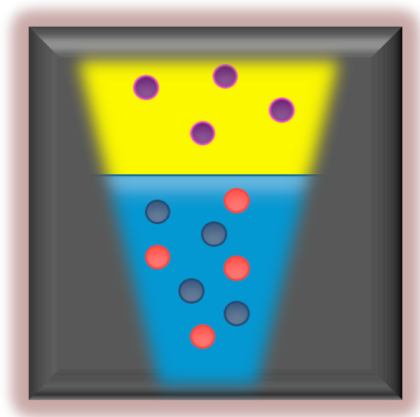
Extracting Ligand

-Partition to aqueous or interfacial region

-Often in excess



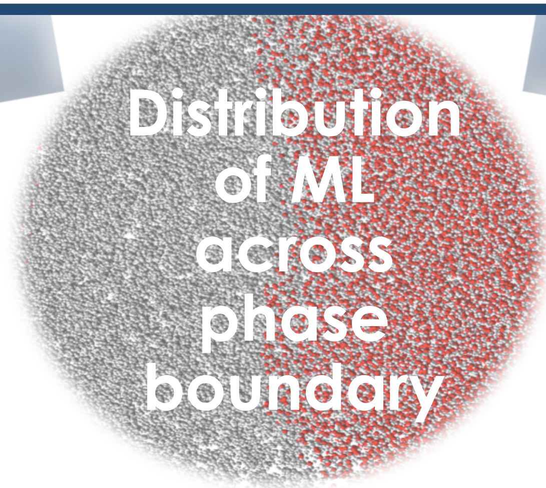
Working Conditions in Extraction



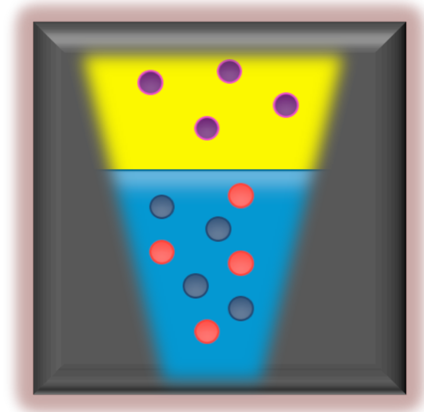
Organic Phase

-single to multicomponent

Goal: Optimize Solvent Extraction Processes By Understanding Multiscale Interactions in Solution and at Interface

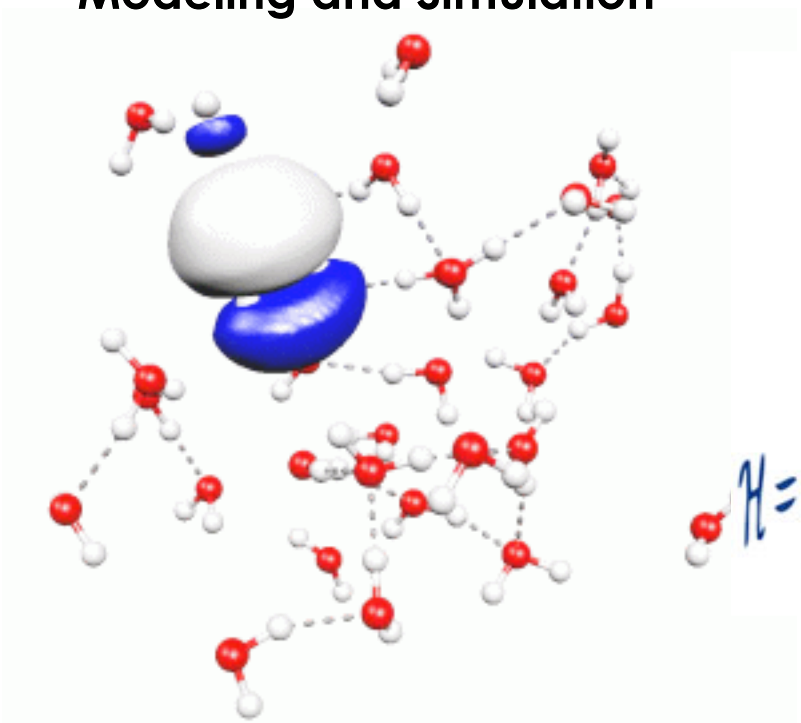


Role of Theory and Simulation



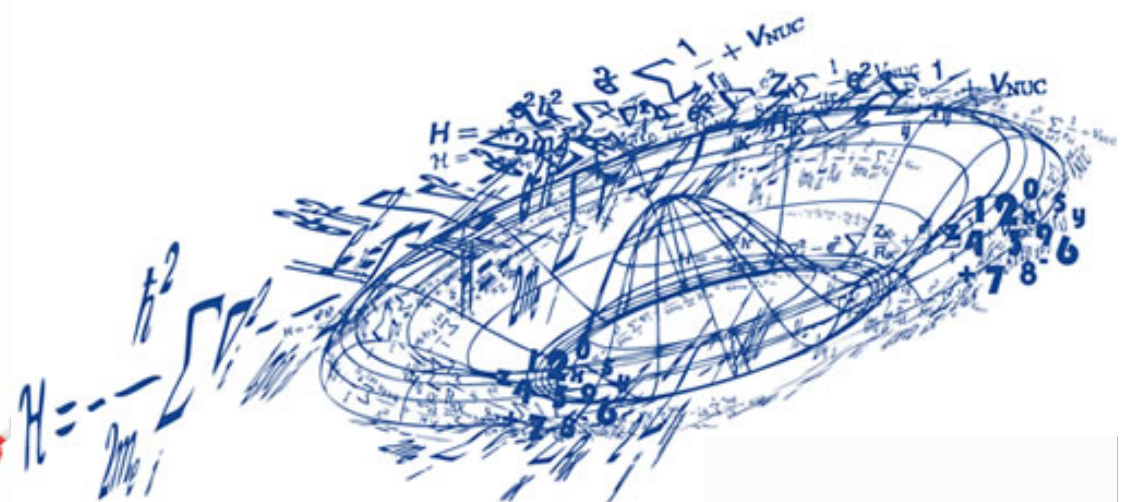
Experimental challenges – deconstructing complex interactions

Modeling and Simulation



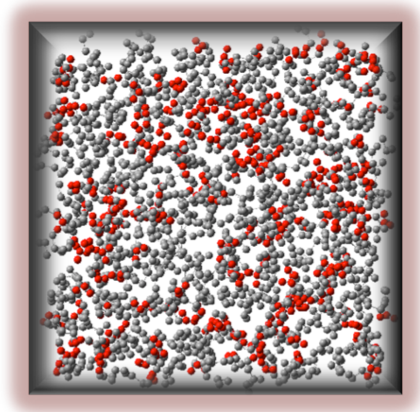
- Employ realistic solution models
- Requires leadership class computing

Theoretical Development



- Complex solutions have complex correlations
- Analyze data in new ways

What Does "Realistic" Mean?



- Multiple solvents
  - Binary, ternary…
- Many types of solutes
  - Ionic strength, ligands, interfacial modifiers
- Realistic concentrations
  - > 10M solute concentrations
- Realistic reactivity
  - Associated with computational method and its approximations
  - Enabling dissociation (Reaxff, ab-initio, quantum molecular dynamics)
  - Herein classical MD (do employ AIMD, just began collaboration with Tom Markland for QMD)
- Realistic time
  - Must accelerate dynamics in some cases

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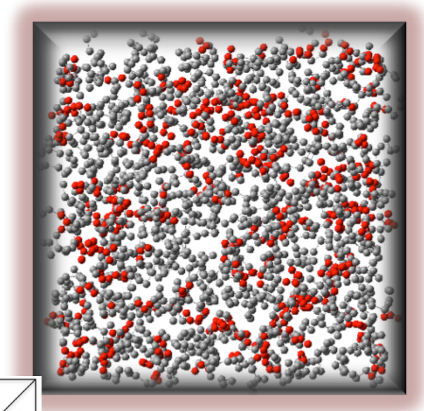
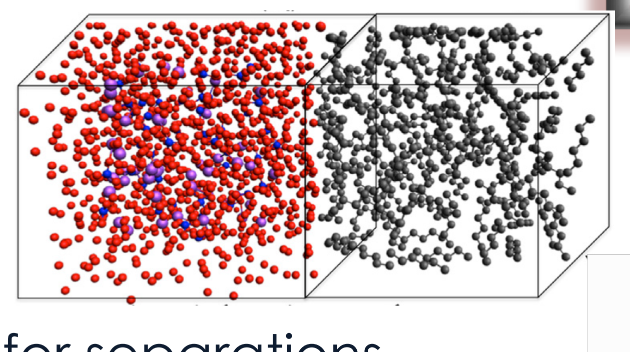
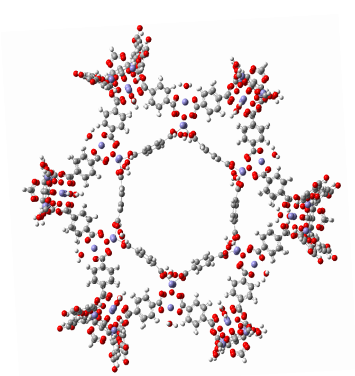
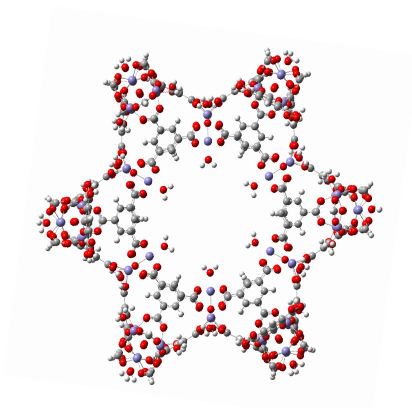


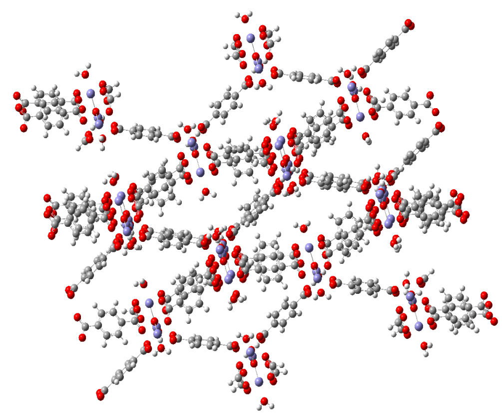
- Typical binary solvent system
  - 10^3 molecules
  - Solutes are often small
  - 10's of ns of simulation



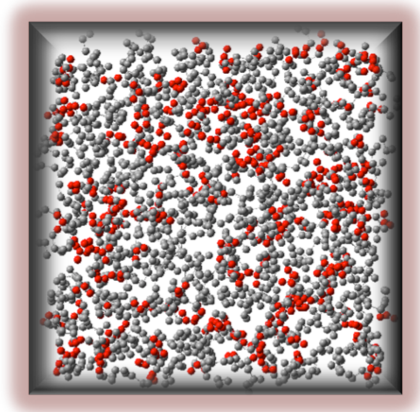
- Solvent Extraction → Materials for separations
  - Solutes are large (1,000 atom clusters)
  - 10^4 molecules
  - Hundreds of ns of simulations





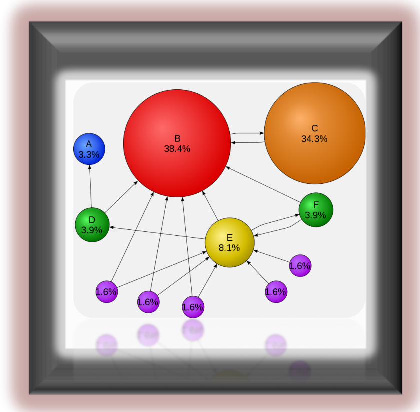


Realistic Simulations Challenge Our Ability to Learn

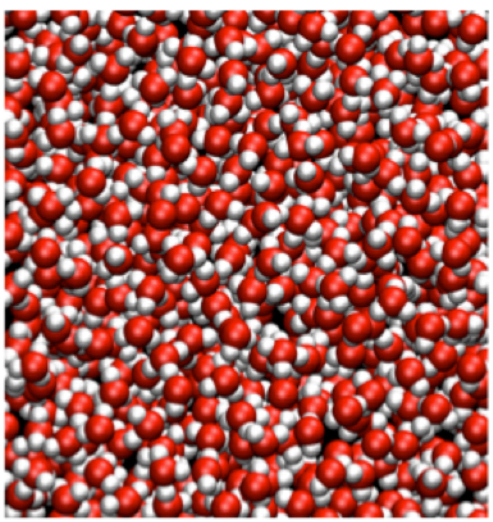
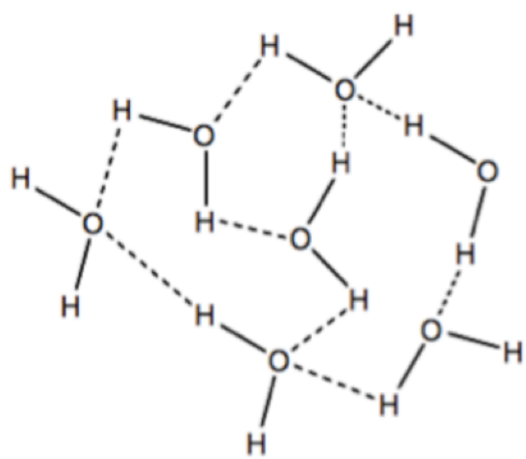
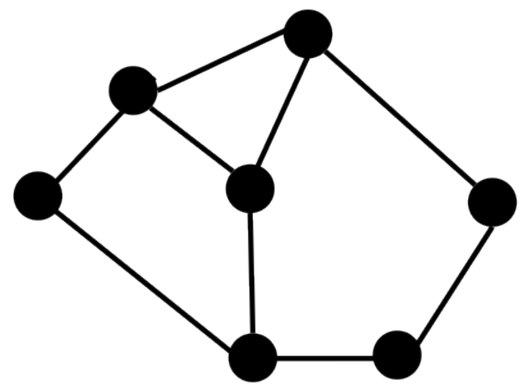


- What are the challenges?
  - Decomposing the average into its subcomponents (speciation)
  - Rare events
  - Quantifying different length and timescale behavior
  - Finding correlations between different length and timescales
  - What specific structural and dynamic features are related to the physical property of interest
- Inhibits predictive capability because we don't have a sound theory of liquids across length and timescales
- Overcoming the challenge (computationally)
  - New computational analyses, chemical theories for thinking about liquids in complex environments

Intermolecular Network Theory

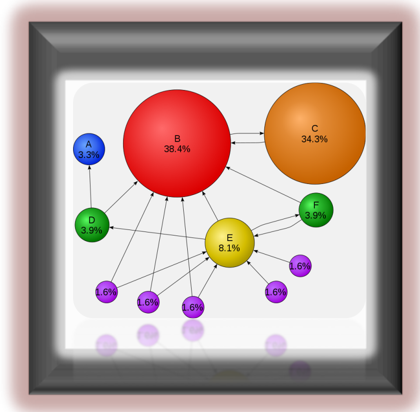


- **Focus upon time-dependent evolution of intermolecular interactions and patterns therein**
- What are the dominant interactions in the liquid?
  - H-bonding, dispersive interactions, ion-ion interactions, etc.
- Create the network of those interactions
  - Data reduction/compression

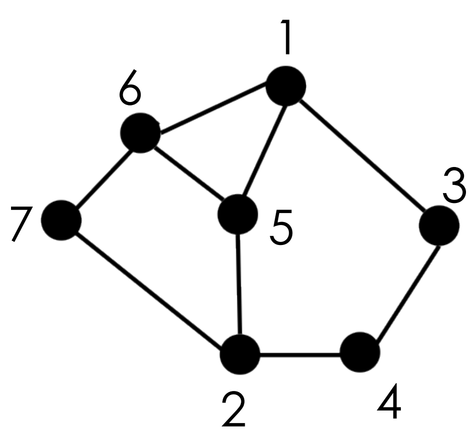
Ozkanlar, A.; Clark, A. E. *J. Comp. Chem.*, **2014**, *35*, 495-505.; Clark, A.E. In *Ann. Rep. Comp. Chem.;* Dixon, D. A., Ed.; **2015**; pp 313–359

Representation of a Network



- The adjacency matrix

$$A_{ij} = \{1,0 \text{ satisfy a criterion for the interaction}$$

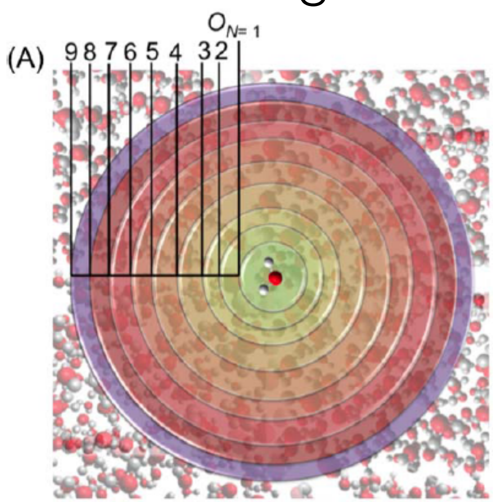


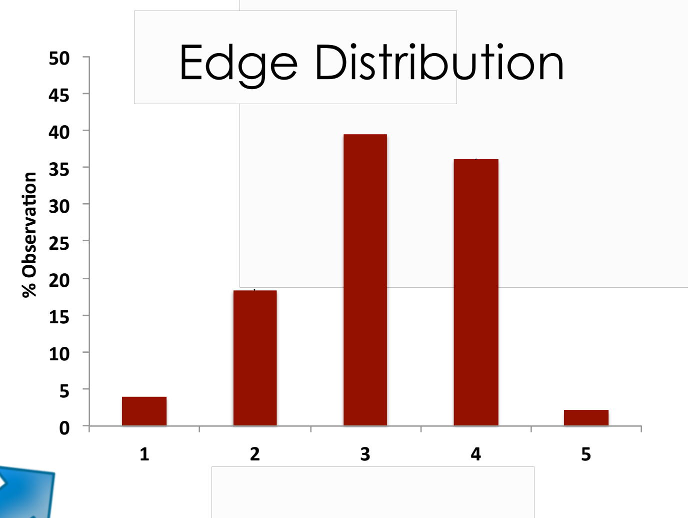
	1	2	3	4	5	6	7
1			1		1	1	
2				1	1		1
3				1			
4							
5						1	
6							1
7							

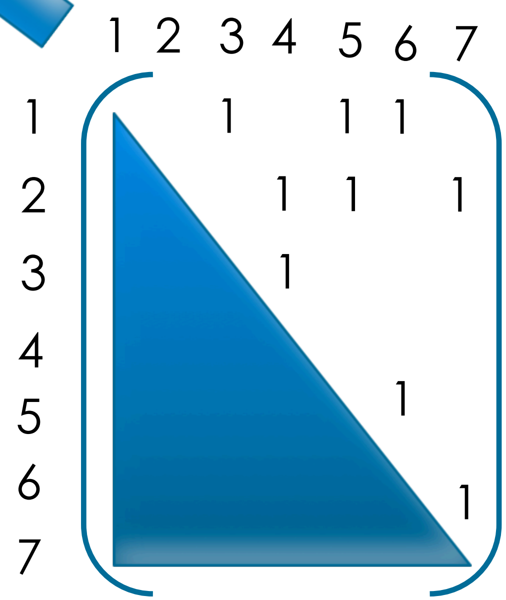
Ozkanlar, A.; Clark, A. E. *J. Comp. Chem.*, **2014**, *35*, 495-505.; Clark, A.E. In *Ann. Rep. Comp. Chem.;* Dixon, D. A., Ed.; **2015**; pp 313–359

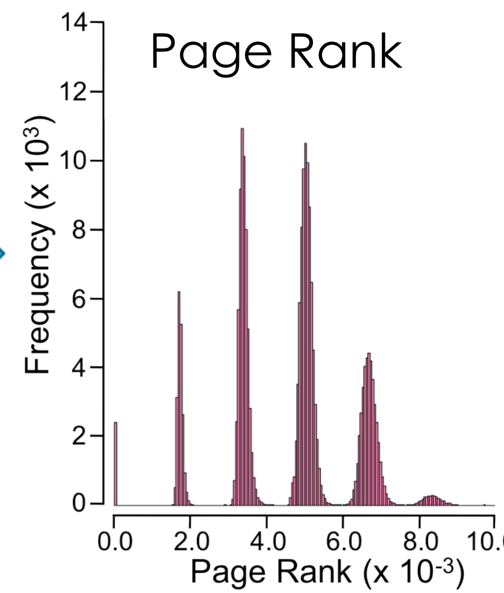
Analysis of a Network

Network Neighborhood

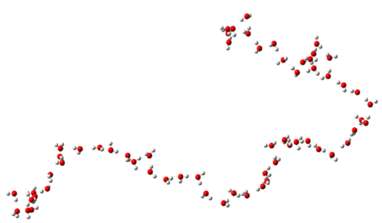








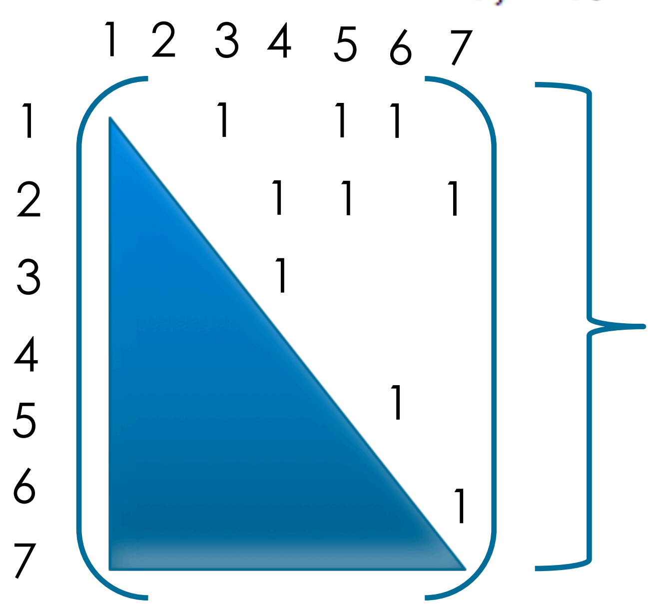
Geodesic Analysis



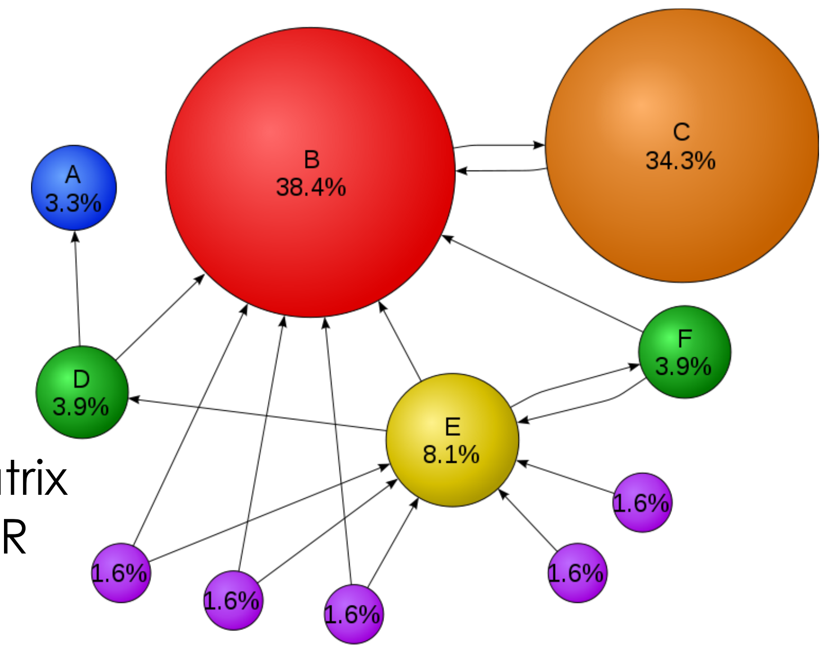
Other Quantities for Local Structure

- PageRank algorithm (Google internet search engine)
- Assigns numerical weighting to each element of a hyperlinked set of

$$PR(p_i) = \frac{1-d}{N} + d \sum_{p_j \in M(p_i)} \frac{PR(p_j)}{L(p_j)}$$



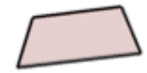
A unique adjacency matrix has a unique PR



Brin, S.; Page, L., In *Proceedings of the 7th International Conference on the World Wide Web (WWW)*. Enslow, P. H.; Ellis, A., Eds. (Elsevier: Amsterdam, 1998), p 107.

Other Quantities for Local Structure

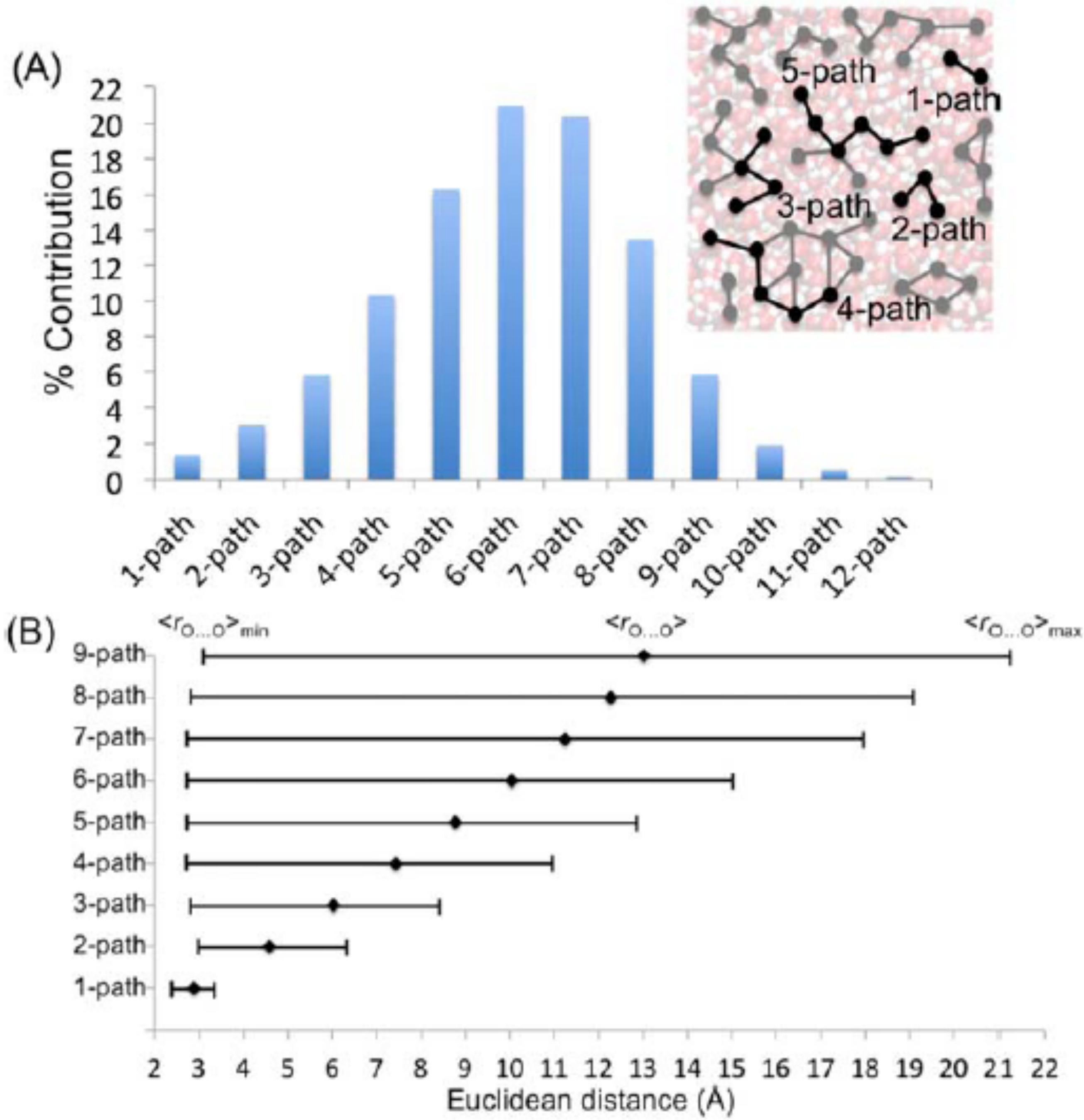
- The coordination about atoms/ ions is well-organized
  - VSEPR, LFT
  - If you consider those as regular polygons, they have unique adjacency matrices
  - Unique PR
  - PR becomes a data-mining tool to search for specific geometric configurations in a system

Number of Vertices	Polygon Name	Shape	PageRank
4	square		0.2441558
4	tetrahedron		0.200000
5	square pyramid		0.1892430
5	trigonal bipyramid		0.1772388
5	wedge		0.2035064
6	octagon		0.1636142
6	pentagonal pyramid		0.1822820
6	trigonal prism		0.1929308

Mooney, B. L.; Corrales, L. R.; Clark, A. E. *J. Phys. Chem. B*, **2012**, *116*, 4263. .; Hudelson, M.; Mooney, B. L.; Clark, A. E., *J. Math. Chem*. **2012**, *50*, 2342

Extended Network Properties – Geodesic analysis

- Dijkstra, or Floyd-Warshall algorithm
- Routing algorithm – basis of MapQuest
- Shortest distances between any two paths using roadways of interactions



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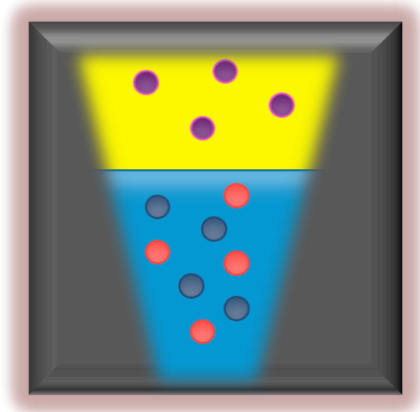
Working Conditions in Extraction



Organic Phase

-single to multicomponent

-solutes acting as modifiers

Aqueous Phase

-High ionic Strength

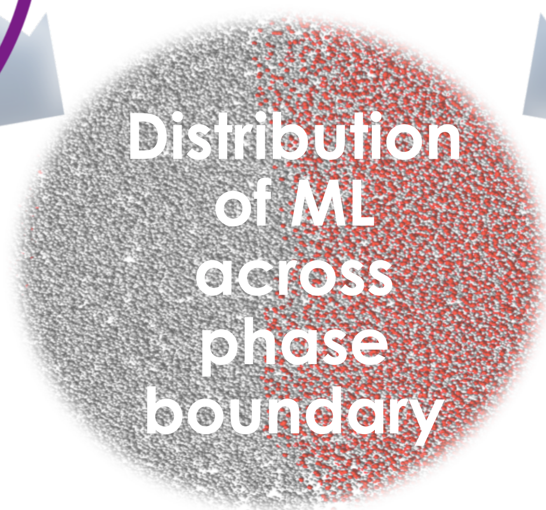
-High acidity

-Complex mixture of metals

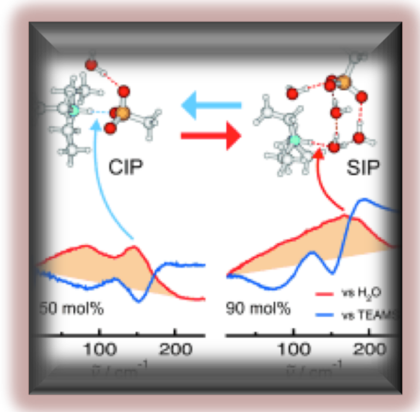
Extracting Ligand

-Partition to aqueous or interfacial region

-Often in excess

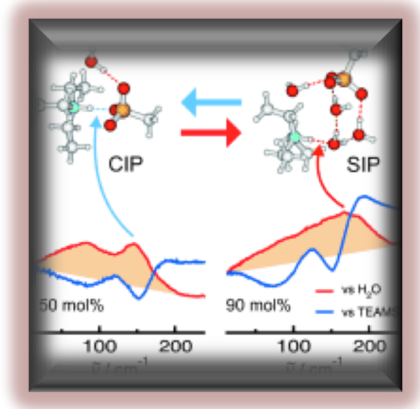


Aqueous Phase



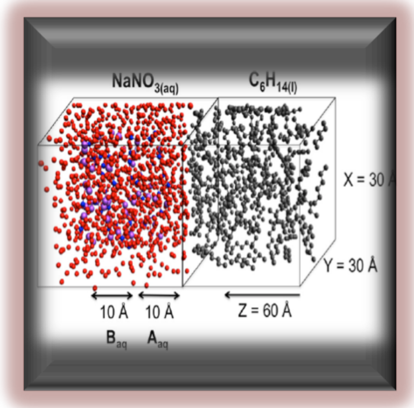
- What are the equilibrium concentrations of different metal ion species?
  - Trivalent U, Np, Pu: *Journal of Chemical Theory and Computation*, **2015**, *11*, 55-63.; *Inorganic Chemistry*, **2015**, *54*, 6216-6225.
- Does the acid anion complex the metal ions of interest?
  - Rh(III): *Inorganic Chemistry,* **2014** *53*, 12315-12322.
- **What is the extent and nature of ion-pairing of the background electrolyte (if any)?**
  - ***Journal of Physical Chemistry B*, 2015 DOI 10.1021/acs.jpcb.5b07492**
- **How does the speciation, acidity, or ion-pairing change in the bulk relative to the interfacial region?**
  - ***Fluid Phase Equilibria*, 2015, DOI 10.1016/j.fluid.2015.07.013.**

Some Interesting Results in the Bulk

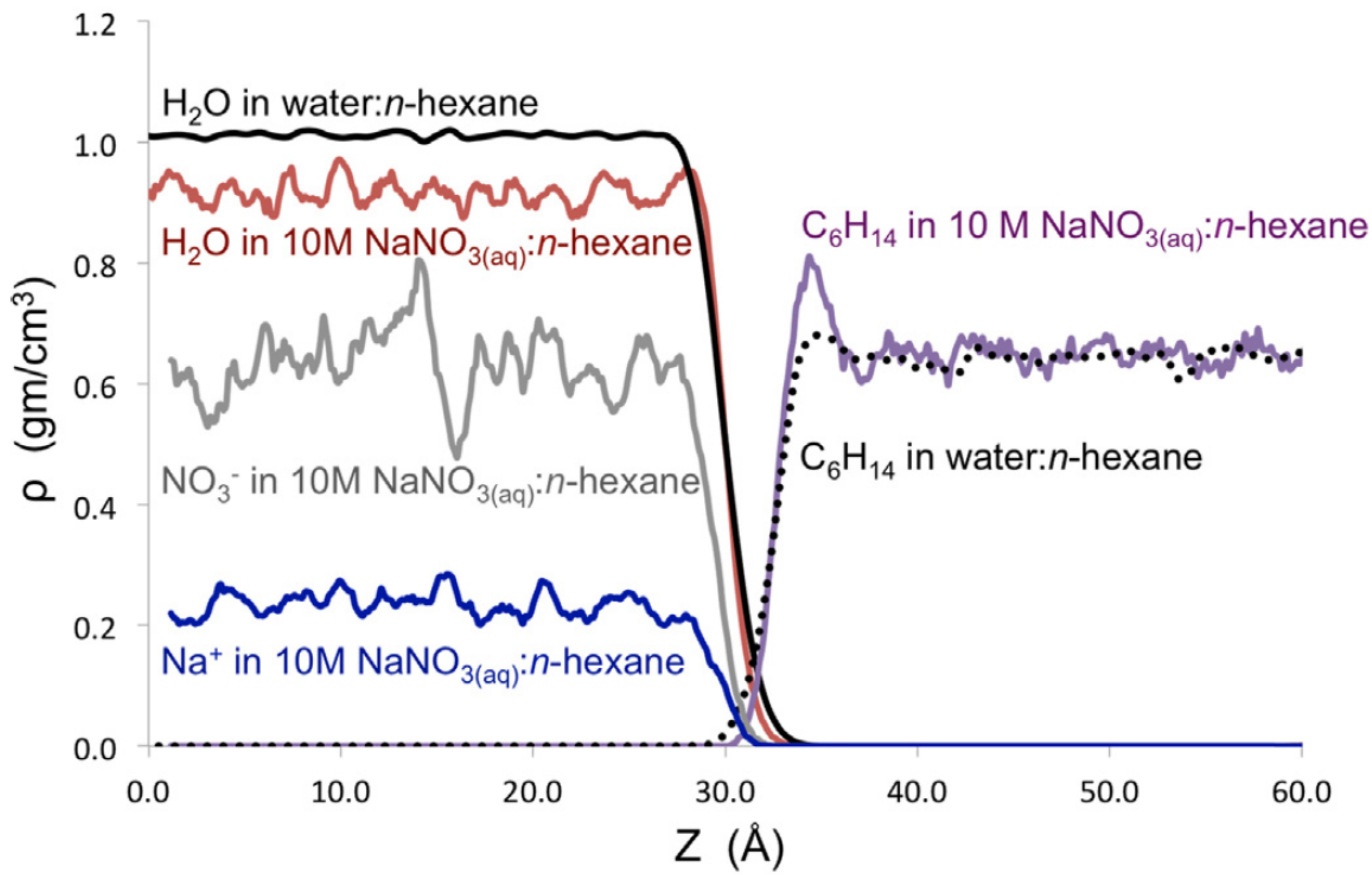


- **Poly-ionic species significant and need to be quantified above 5M**
- **Solution composition can alter the rate of ion-pair formation (kinetic restriction)**
- H-bond structure and dynamics of solution appear to influence dynamics of 1st solvation shell dynamics of simple ions
  - Higher network connectivity and longer dynamics retard exchange events about ions
  - Rate of CIP formation should be altered by change in exchange rate caused by kinetic restriction of solvent AND changes in metal-solvent binding energies.
  - May extend to rate of poly-ionic species formation as well

Ion-Pairing Near Aqueous:Organic Interface



- Change in ion distribution near interface



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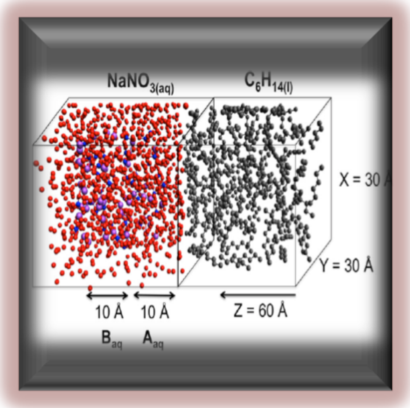

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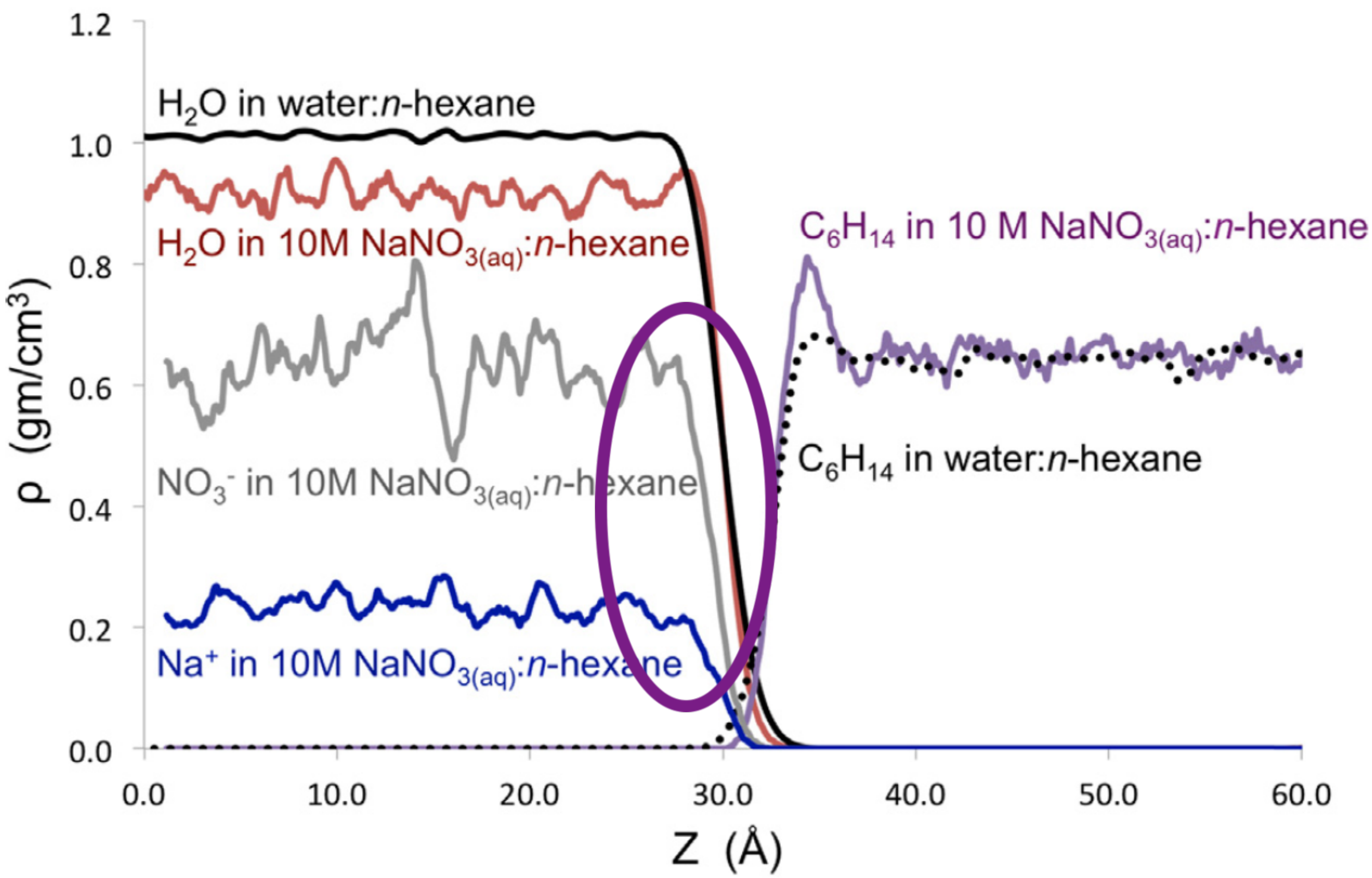

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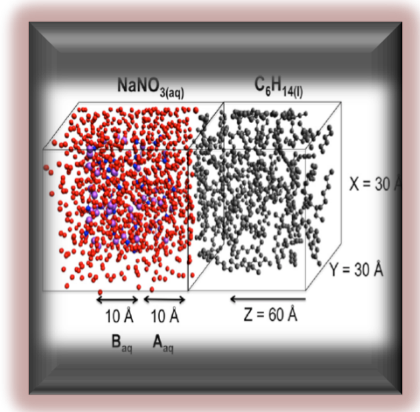
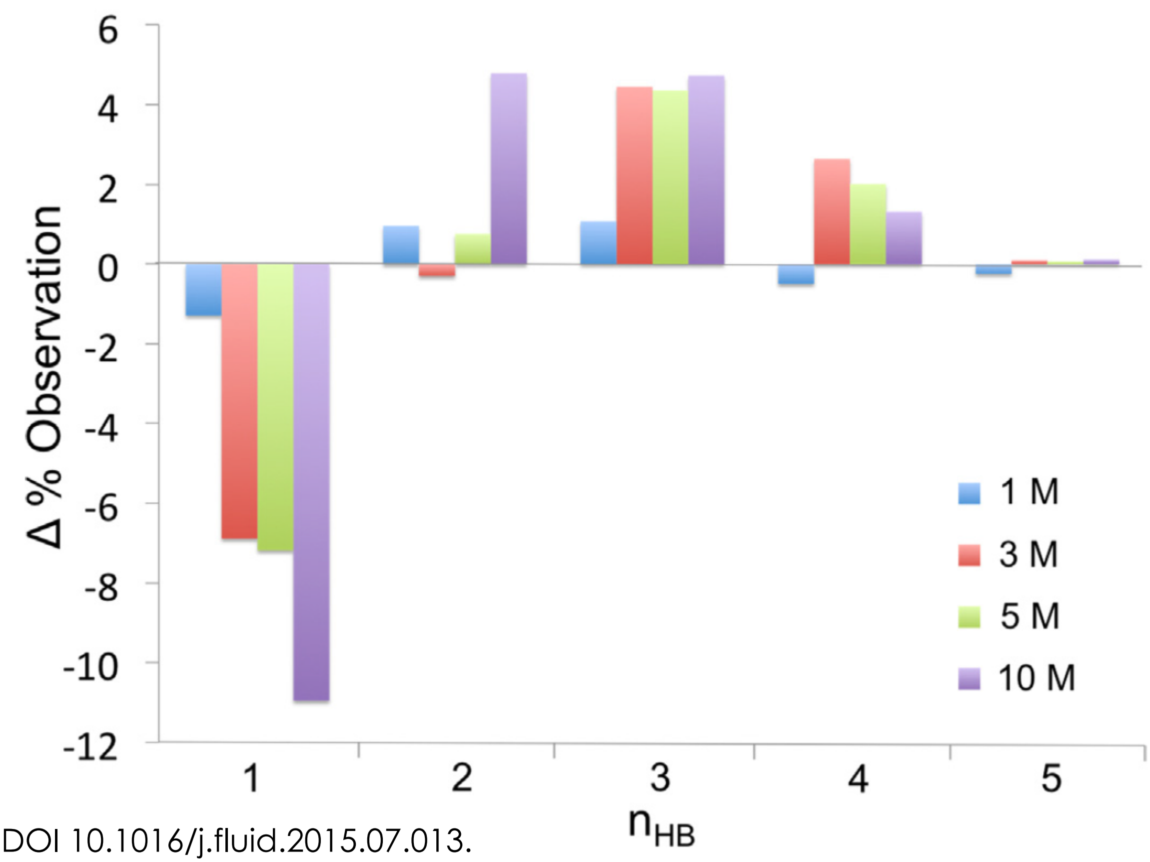


- Growth of H-bonding in interfacial region caused by H_2O being less tied up in ion solvation



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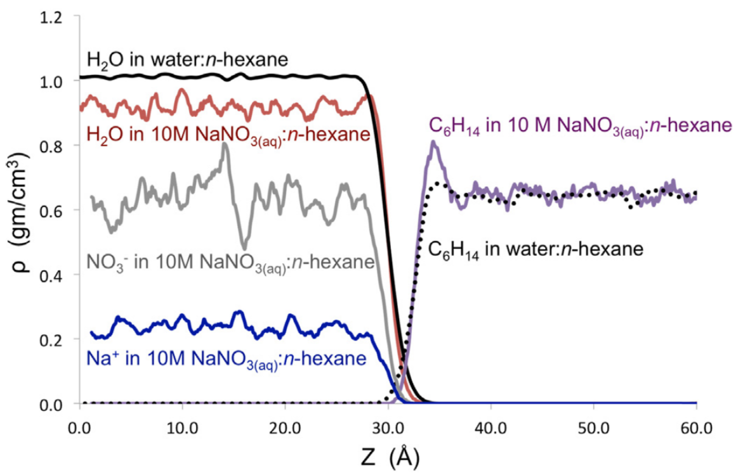
Modulation of Interfacial Tension



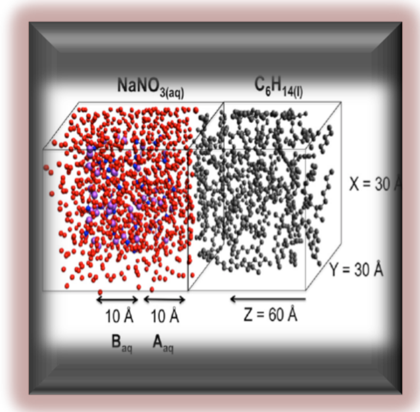
$$\Psi(z) = \frac{2}{\rho_l - \rho_v}\left(\rho(z) - \frac{\rho_l + \rho_v}{2}\right)$$

$$\Psi_e(z) = \mathrm{erf}\left(\sqrt{\pi}\left(\frac{z - z_0}{w_e}\right)\right)$$

- Huge increase in interfacial tension in 10 M $NaNO_3$

$NaNO_3$ (M)	γ_e (dyne/cm)	w_c (Å)
0	46.3 (43.9 [27], 50.0 [25,26])	1.37
1	42.05 ± 1.99	1.25 ± 0.03
3	45.37 ± 0.32	1.20 ± 0.004
5	49.63 ± 0.88	1.15 ± 0.01
10	83.55 ± 0.19	0.89 ± 0.001

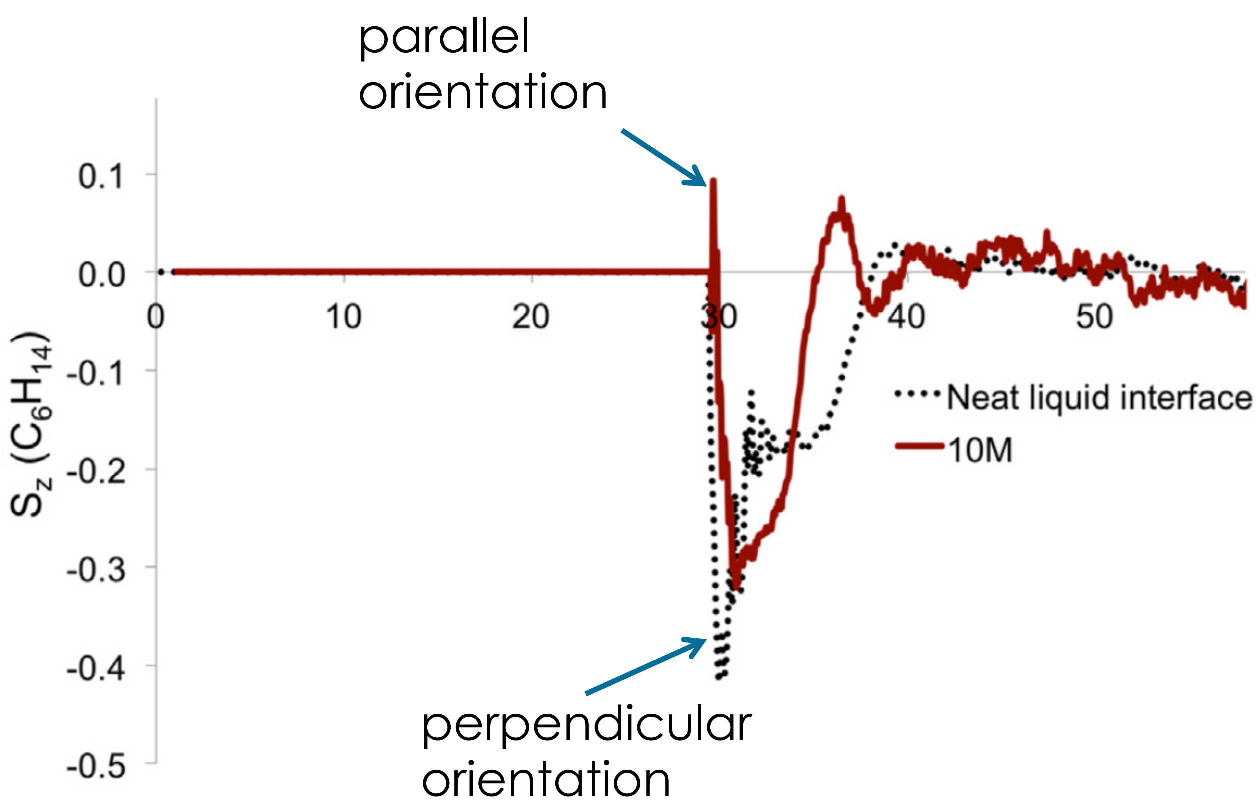
Modulation of Interfacial Tension



- Increased interfacial tension correlated with change in hexane orientation correlated with high aqueous ionic strength

$$S_z = \frac{1}{2(3\langle\cos\theta^2\rangle - 1)}$$

= -0.5 -> perpendicular
= 1 -> parallel



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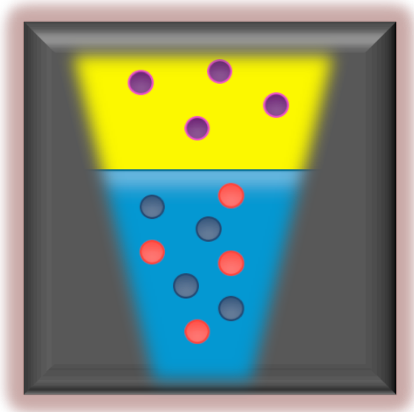

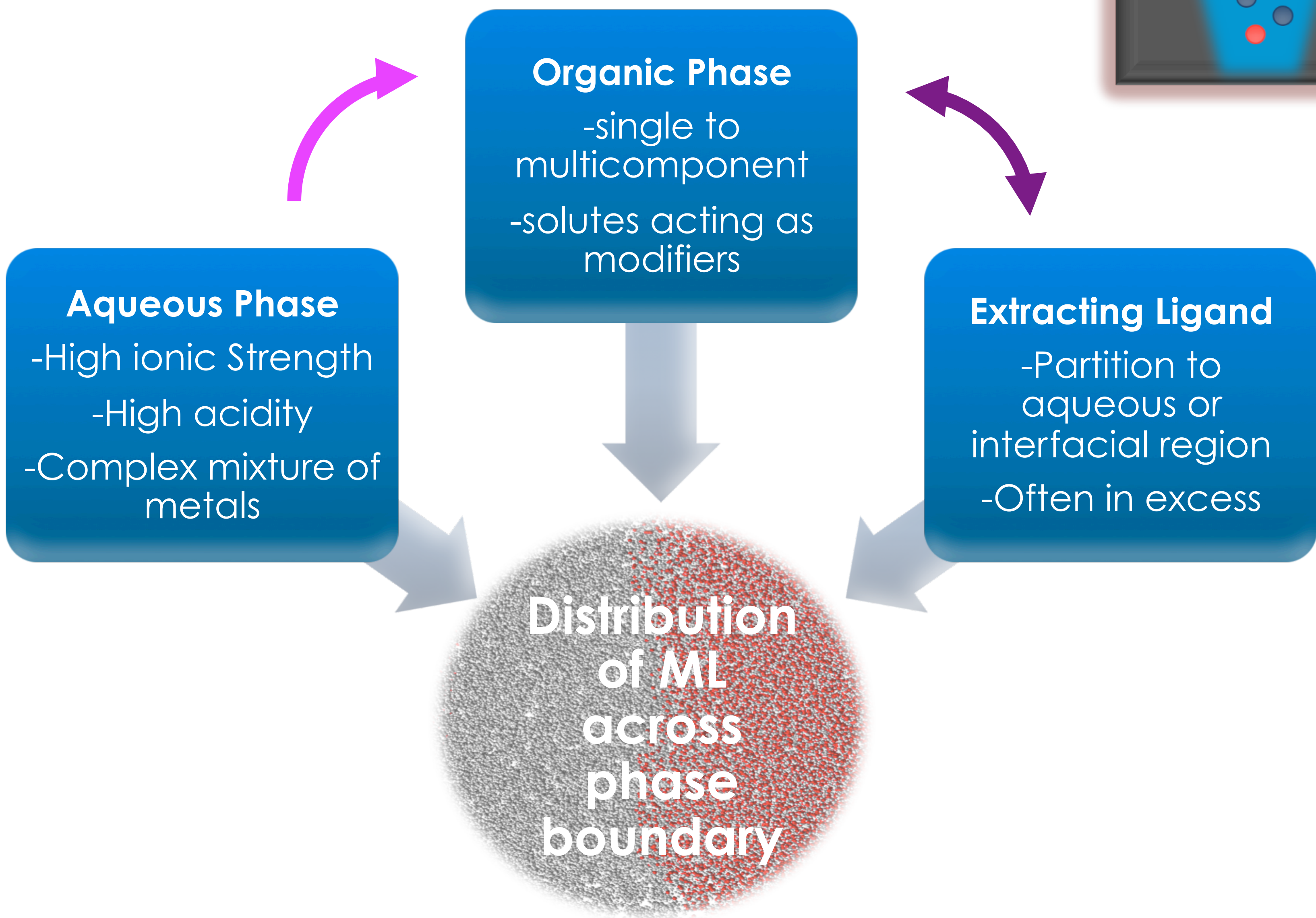

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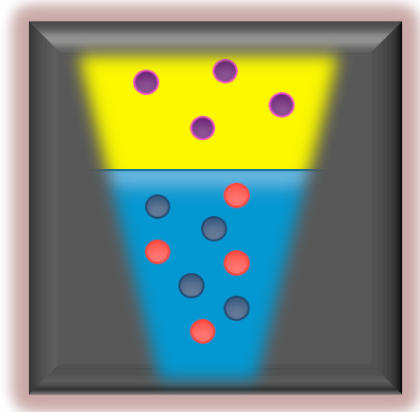

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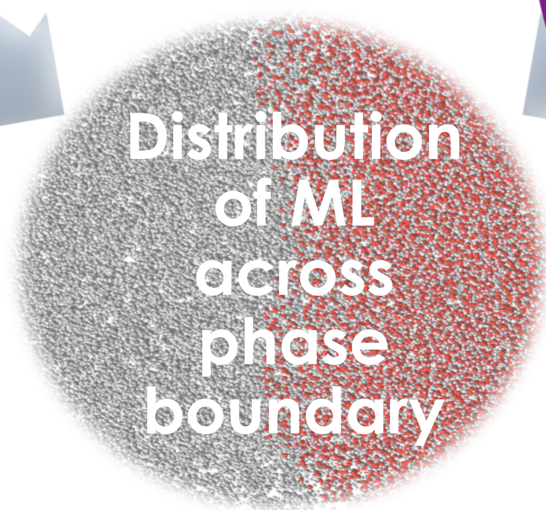
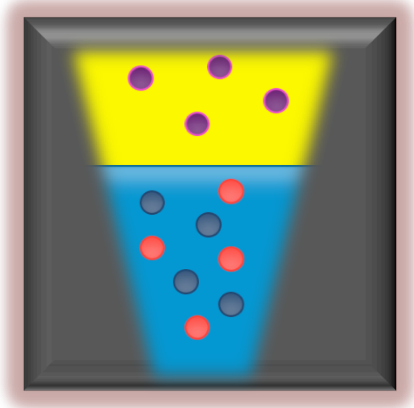


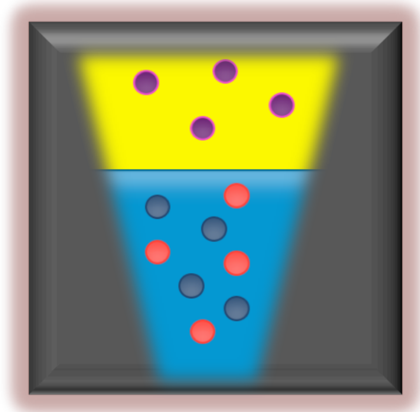
Organic Phase and Extractants



- How does the packing ability or shape of organic solvent influence interfacial properties?
  - *Phys.Chem.Chem.Phys.*, 16, 12475 **(2014)**

- How do solutes in the organic phase influence orientation of organic solvent -> also correlated with interfacial tension?

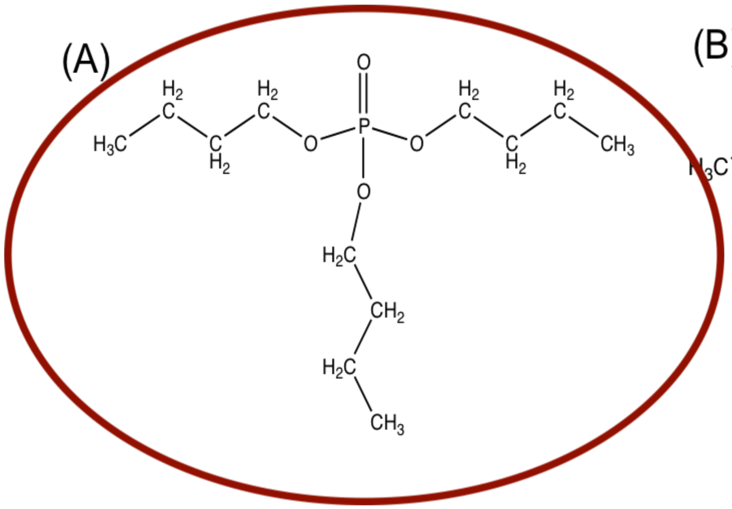
- What is the extent of dynamic motion of solvent and solutes across interface?
  - *Journal of Chemical Physics* 142 , 104707 **(2015)**



Interfacial Tension

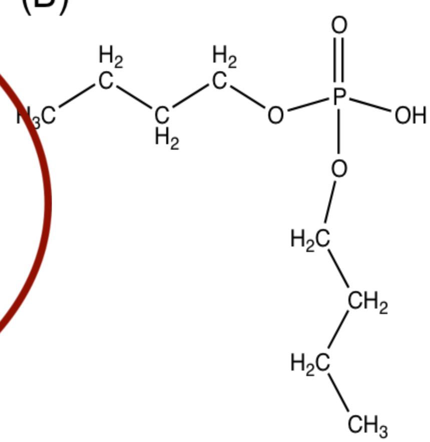
- Presence of an ampiphilic solute at the interface

(A)



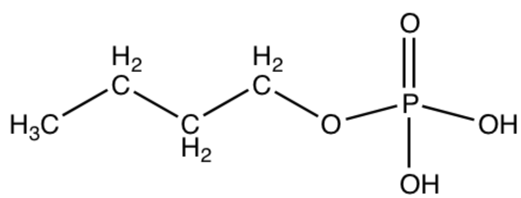
tri-butyl phosphate
(TBP)

(B)



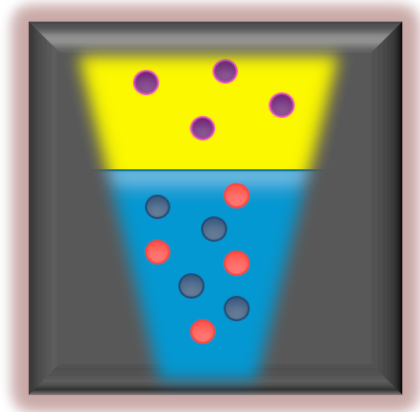
hydrogen di-butyl phosphate
(HDBP)

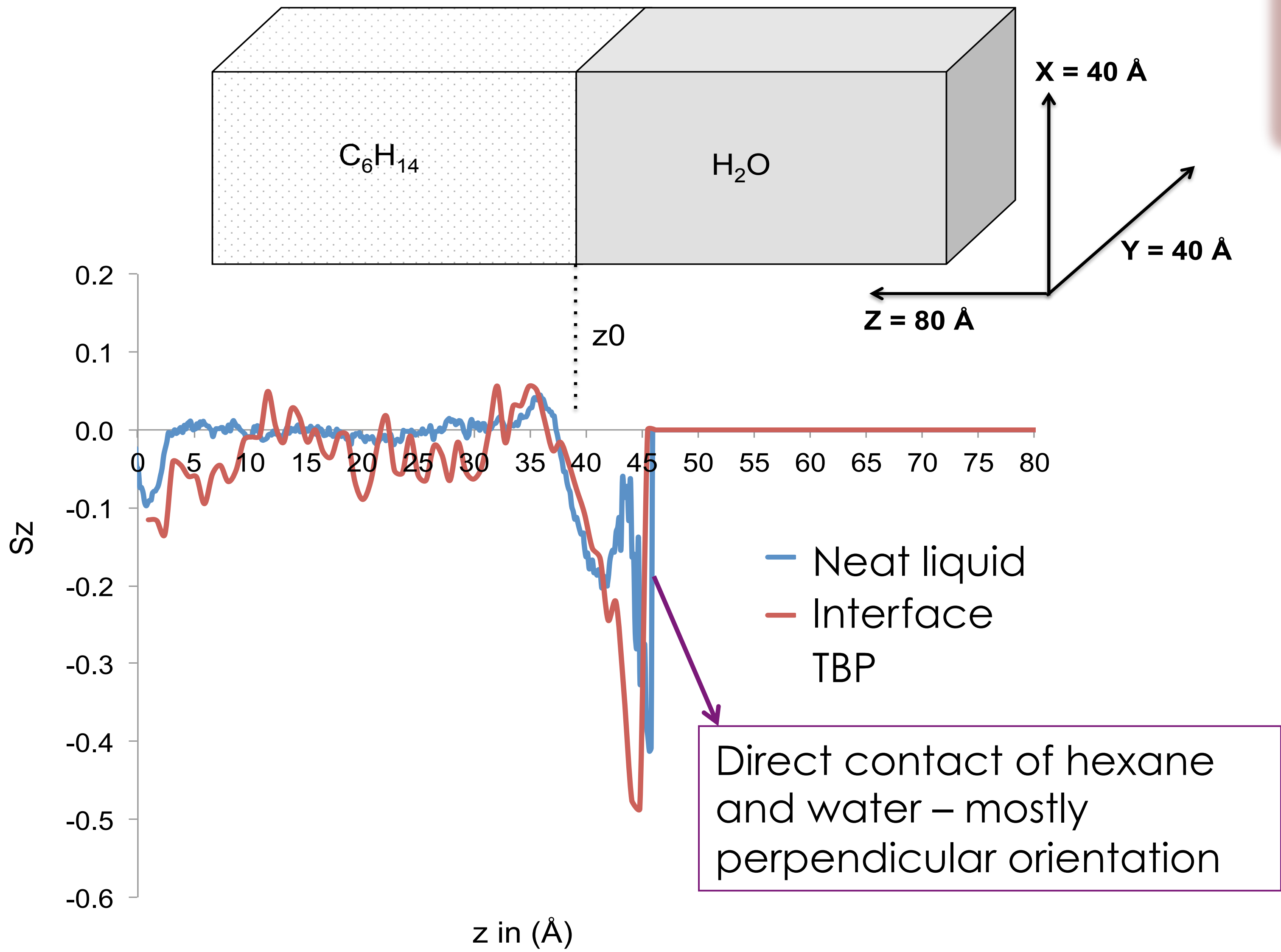
(C)



di-hydrogen mono-butyl phosphate
(H_2MBP)

Hexane Orientation with TBP at the Interface





Y. Ghadar, P. Parmar, A. C. Samuels and A. E. Clark, J. Chem. Phys. 142, 104707, 2015

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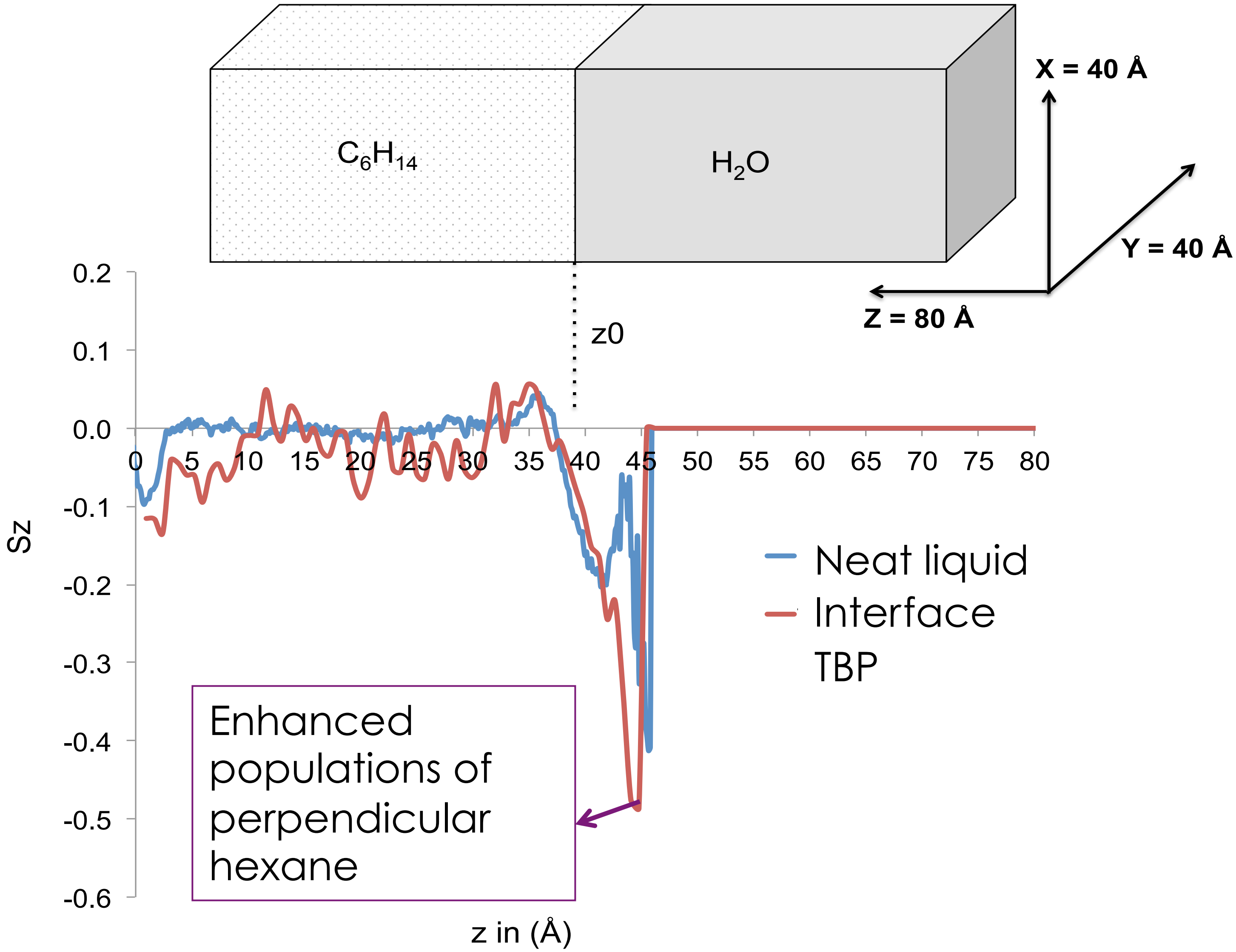

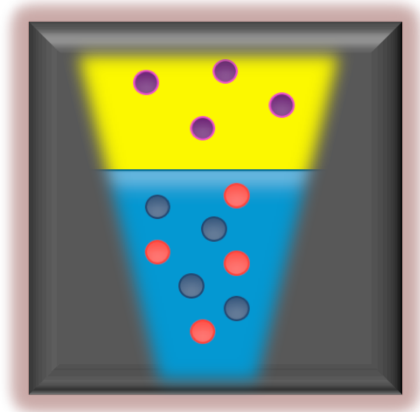

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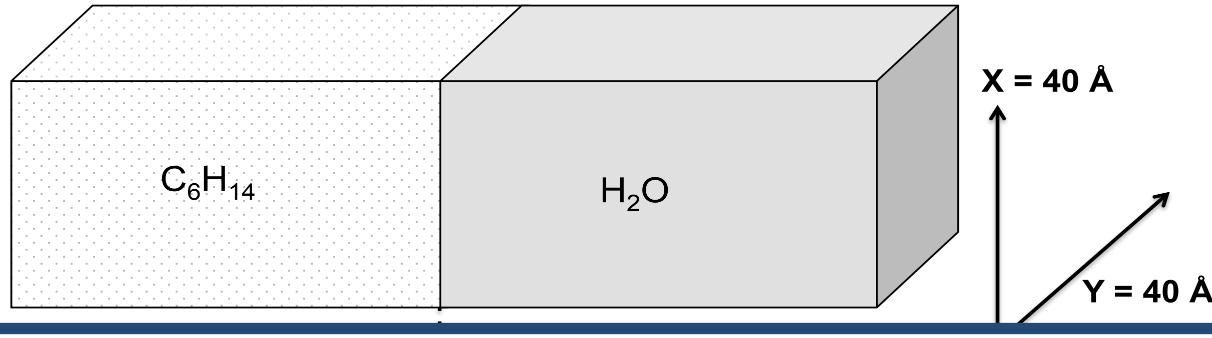
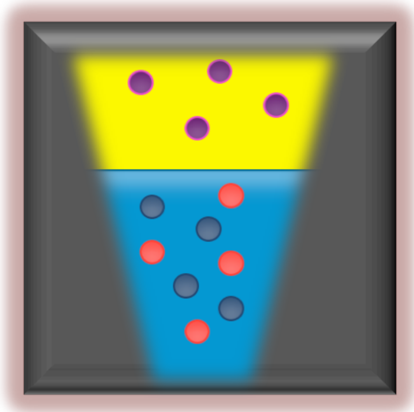
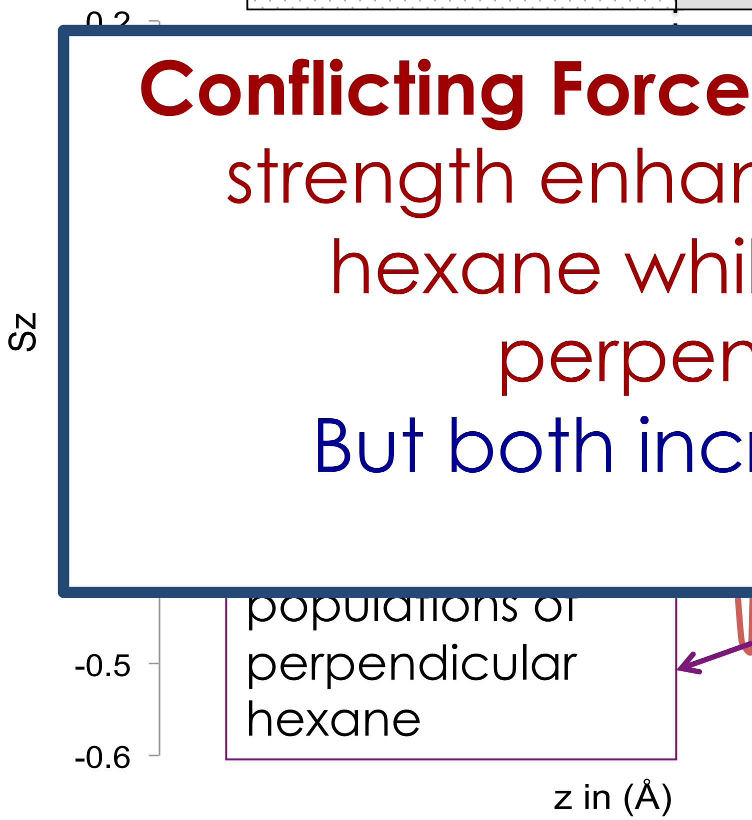




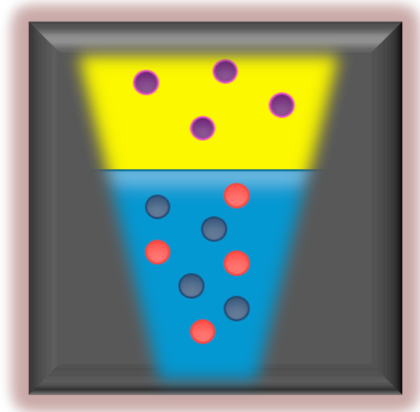


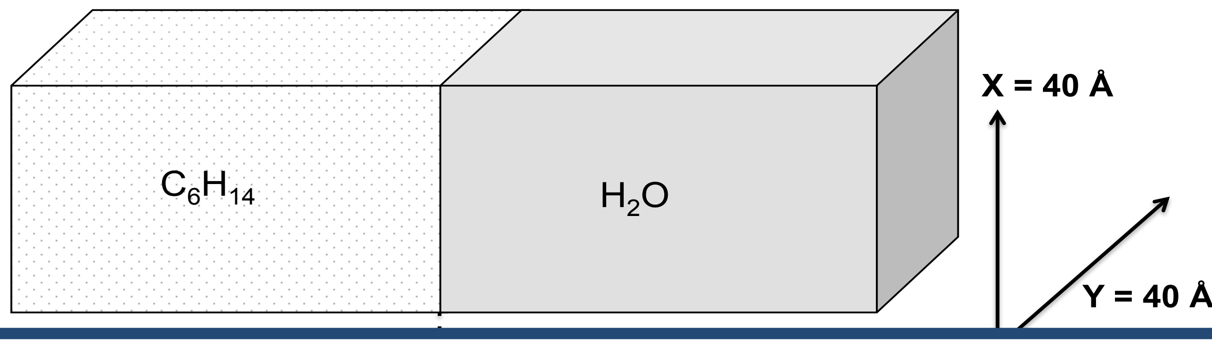
Conflicting Forces at Interface: Aqueous ionic strength enhances parallel orientation of hexane while solutes can enhance perpendicular orientation

But both increase interfacial tension

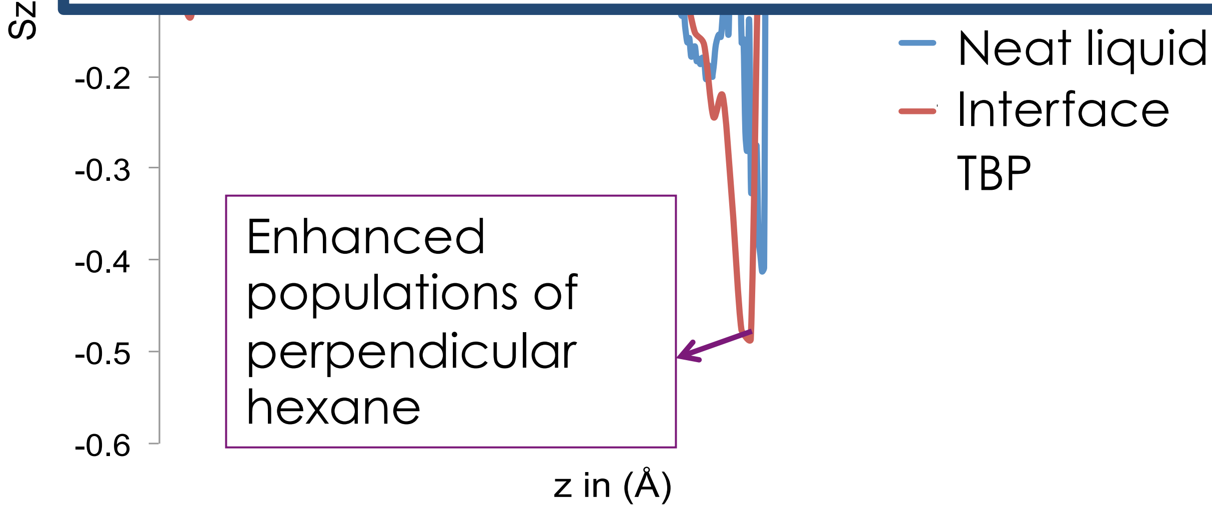
Y. Ghadar, P. Parmar, A. C. Samuels and A. E. Clark, J. Chem. Phys. 142, 104707, 2015

Hexane Orientation with TBP at the Interface





How does this alter transport across phase boundary?



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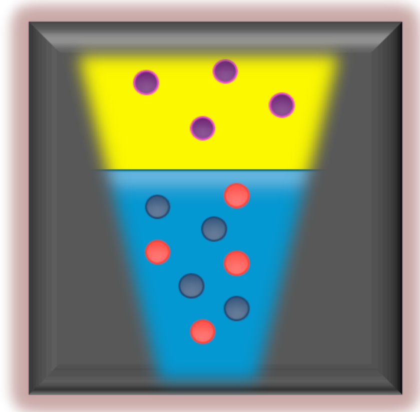
Working Conditions in Extraction



Organic Phase

-single to multicomponent

-solutes acting as modifiers

Aqueous Phase

-High ionic Strength

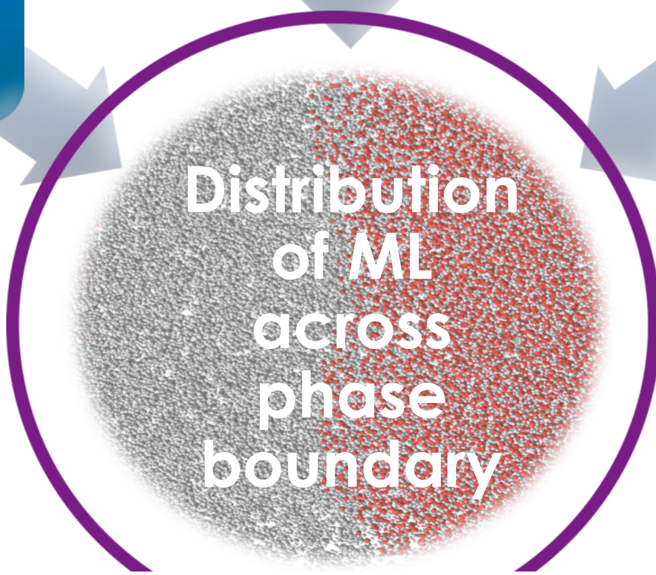
-High acidity

-Complex mixture of metals

Extracting Ligand

-Partition to aqueous or interfacial region

-Often in excess



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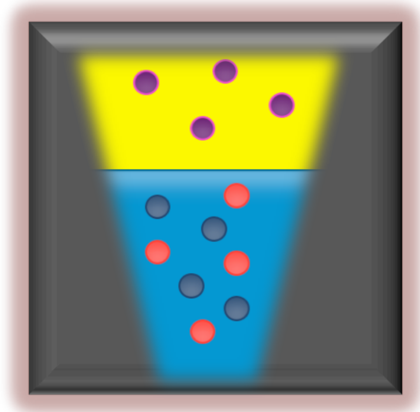

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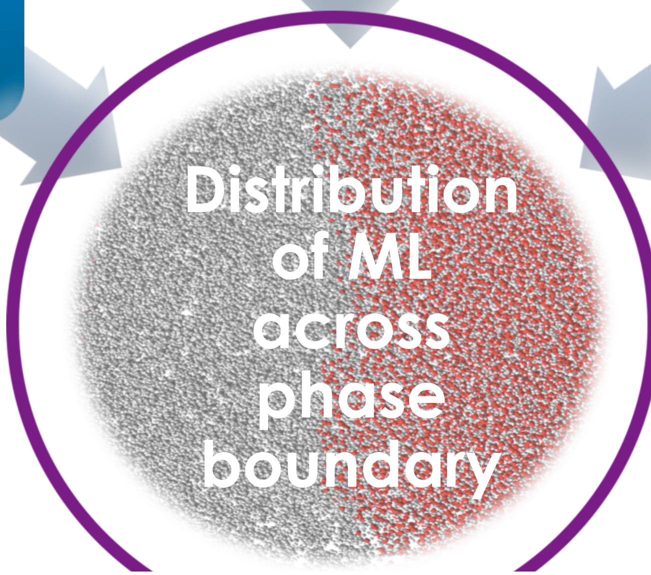
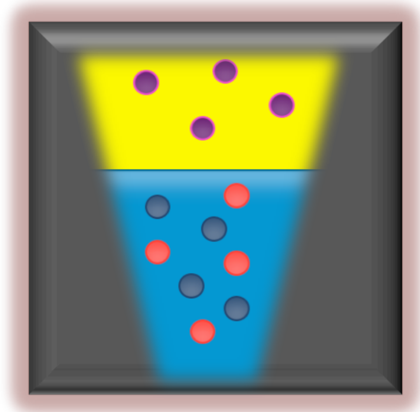
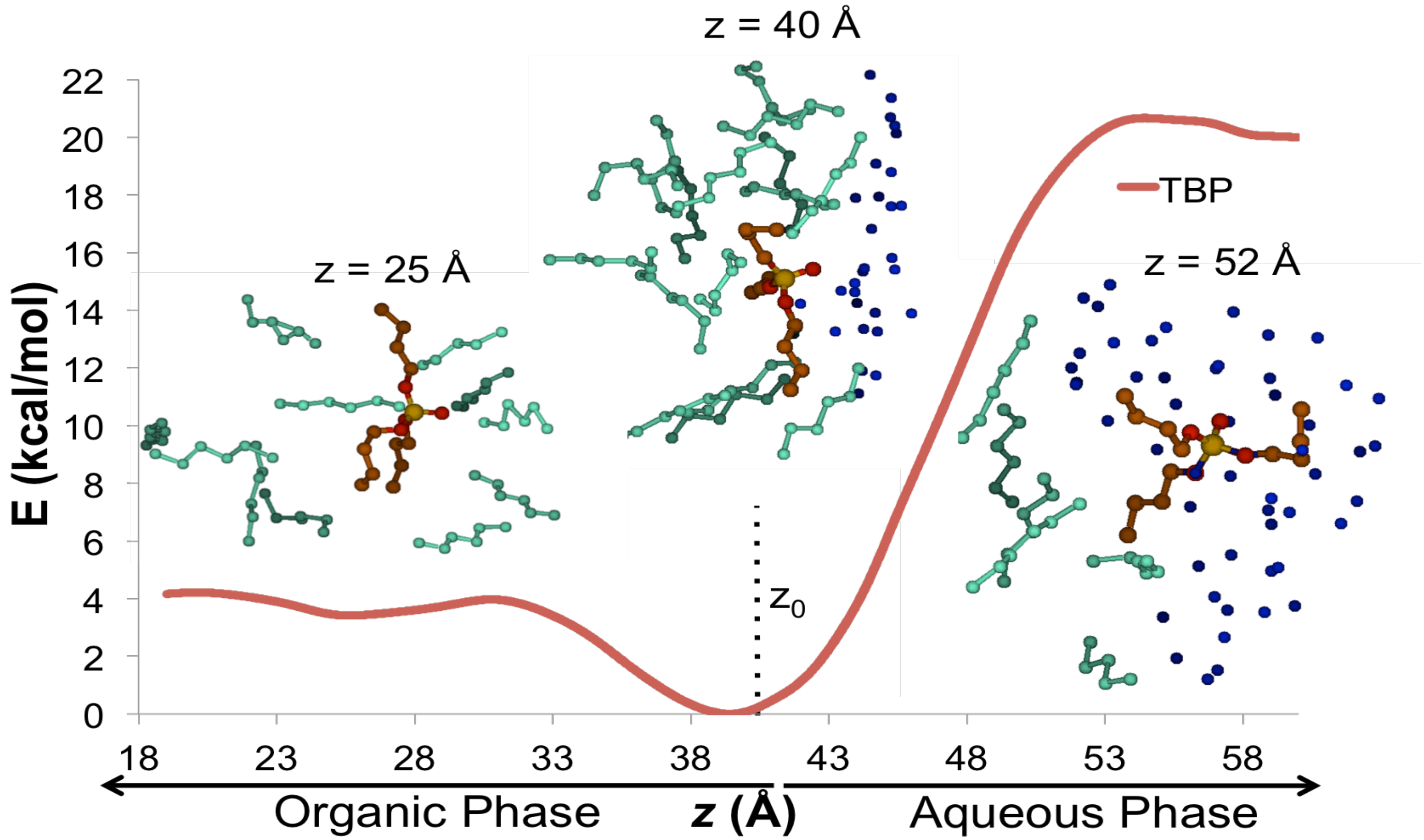


- **Relative free energies of solvation in Aq vs. organic phase**
- **Ease of transport across interface**

Measurement of Permeability?

- **Potential of mean force**
- Dragging solute across phase boundary





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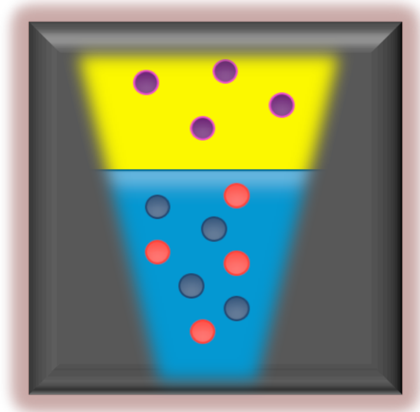
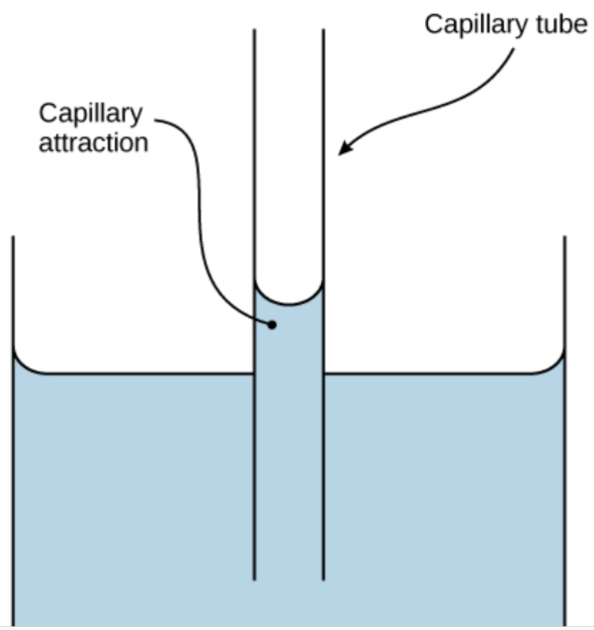


- **Relationship of permeability with solvent miscibility and interfacial tension**
- Liquid:vapor analogue -> Kelvin Equation



$$\ln \frac{p}{p_0} = -\frac{2\gamma V_m}{rRT}$$

Partial pressure is related to surface tension and radius of curvature

Sir William Thomson (1871) Philosophical Magazine, series 4, *42, 448-452.*; Skinner, L. M.; Sambles, J. R. Aerosol Sci 3 (1972) 199-210.; McElroy, P. J. J. Colloid Interface Sci. 72 (1979) 147-149;

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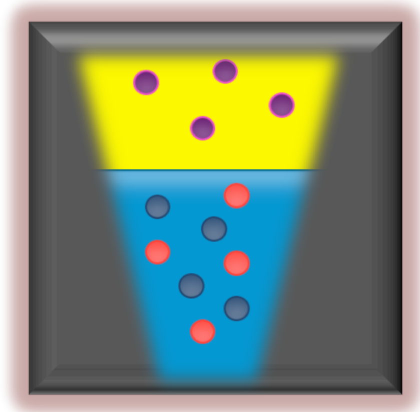

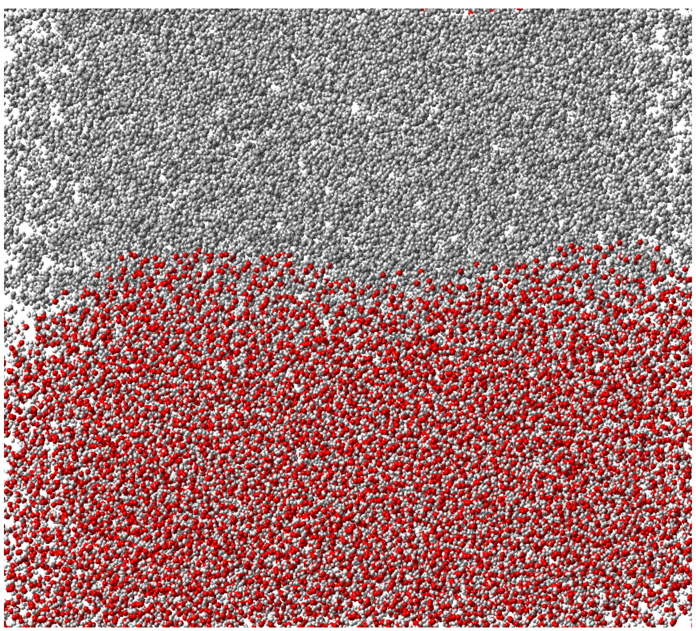

$$\ln \frac{p}{p_0} = -\frac{2\gamma V_m}{rRT}$$

Concentration of co-solvents on either side of the phase boundary should be related to interfacial tension (and perhaps length-scale of capillary waves)

Concentration is easily measured with INT

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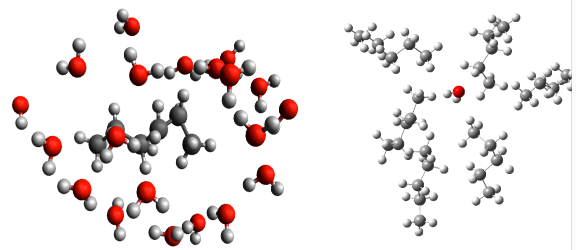
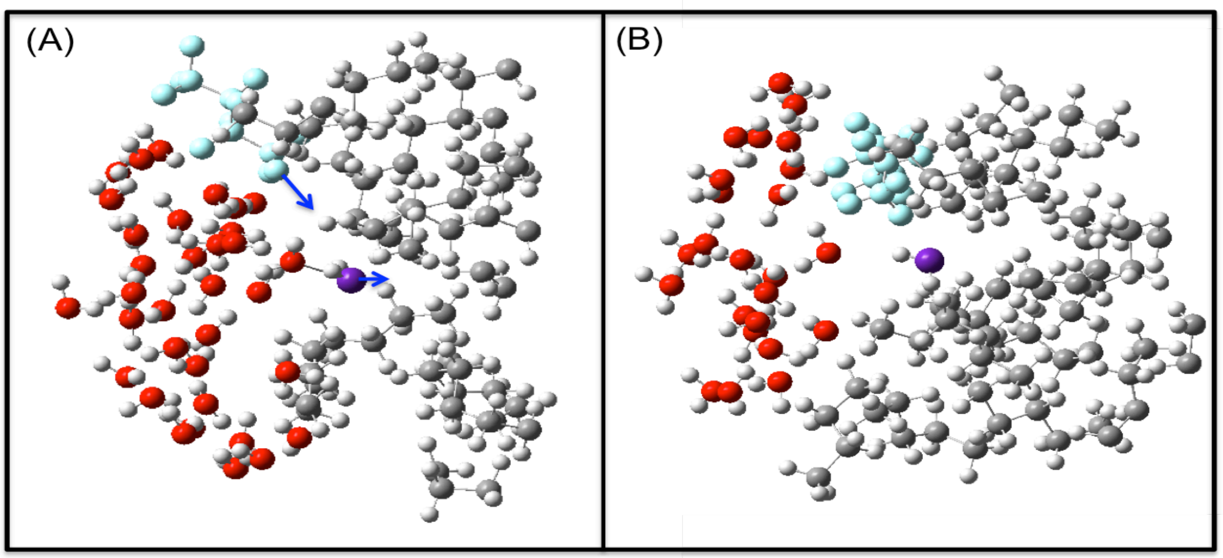
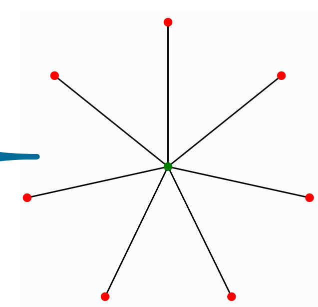
Microsolvation



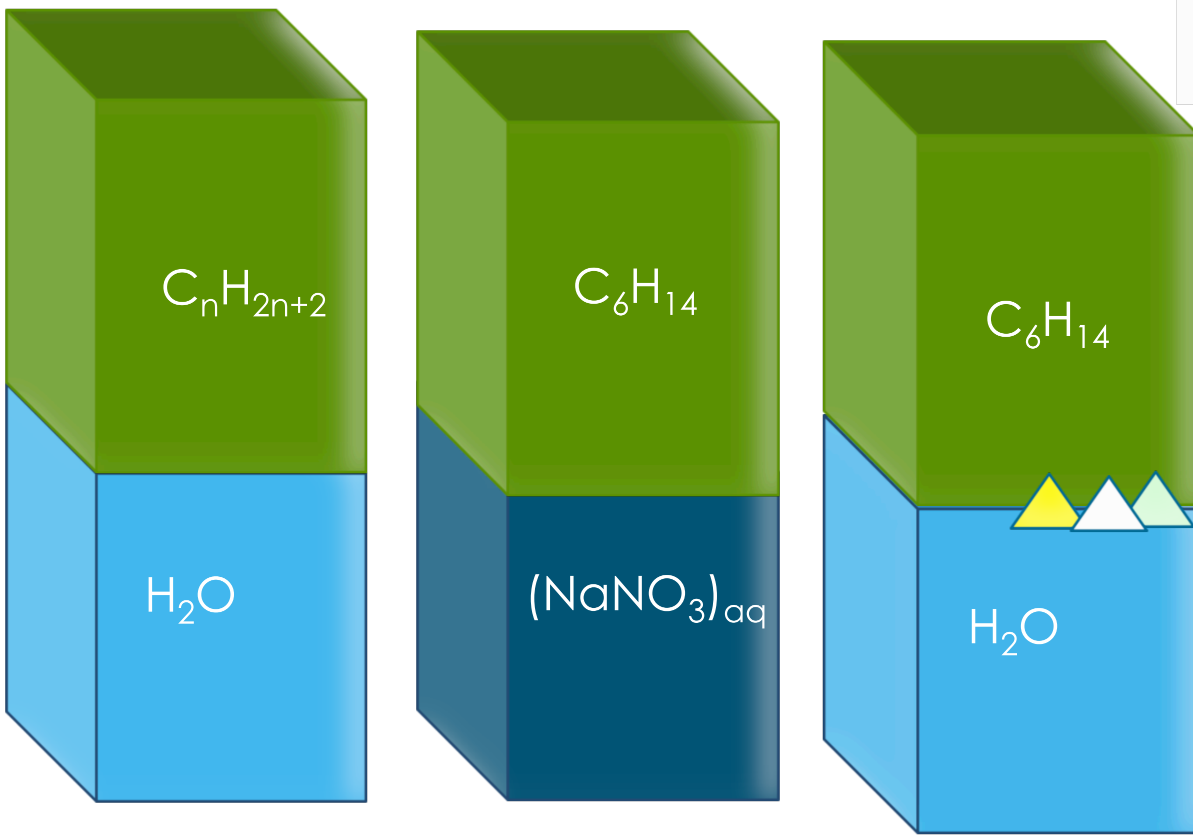
- Microsolvation is an event where two liquids solvate each other
  - Rarity of this event (or thermodynamics of co-solvation) leads to formation of phase boundary
  - We believe that this is related to permeability/transport





Frank H. S., Evans M. W., J. Chem. Phys. 13(11), 507, (1945)
Ghadar Y., and Clark A.E., Phys. Chem.Chem. Phys. 16, 12475, (2014)

Solutions studied

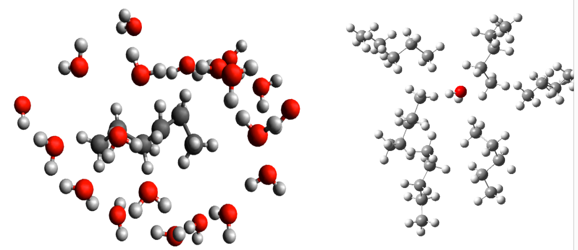


- Water:organic
  - n-Pentane
  - Neopentane
  - n-Hexane

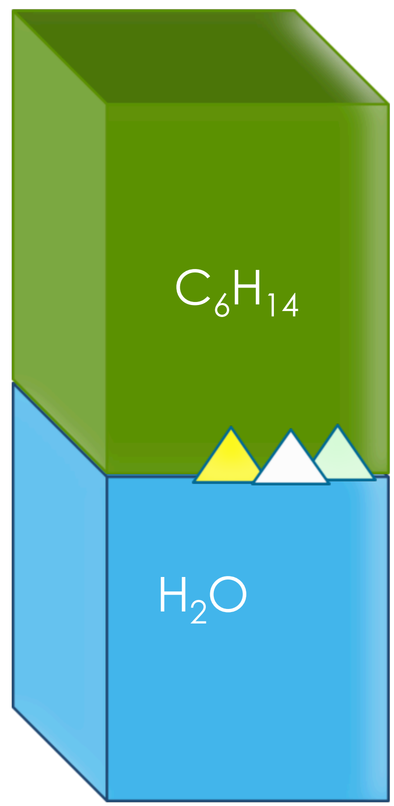
0-10 M

Amphiphilic
Solute (TBP, HCBP, MBP)

Microsolvation

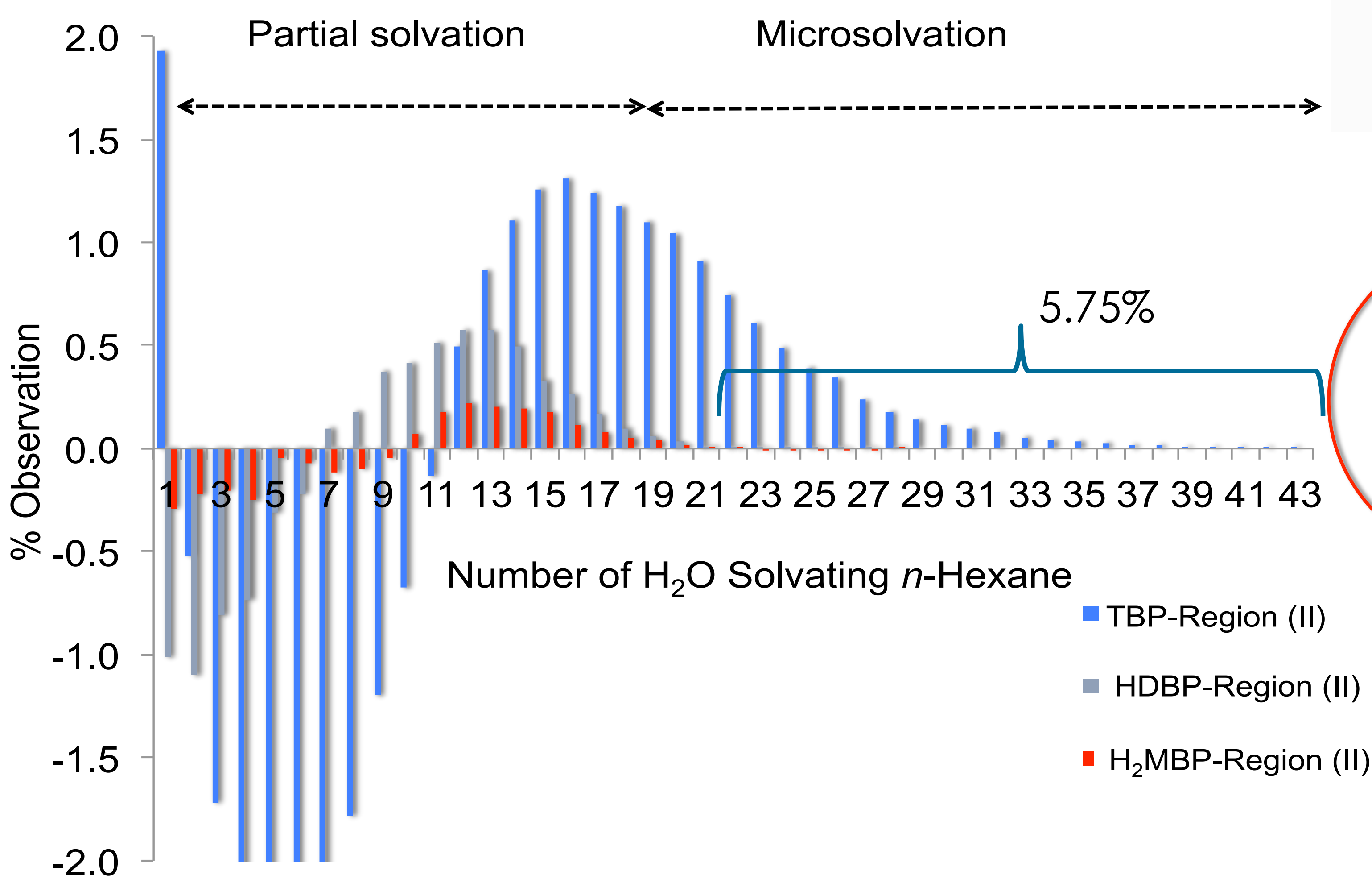


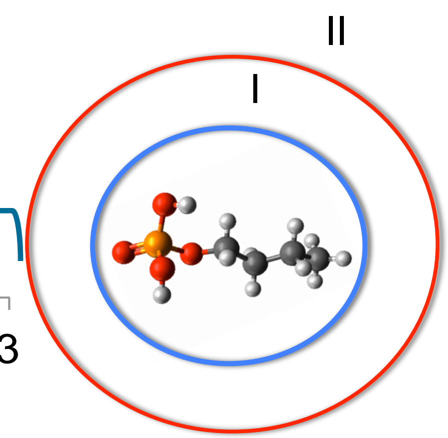
- Despite huge changes in interfacial tension as a function of solution conditions…..
  - only 1 system exhibited large changes in microsolvation/co-solvent concentration
  - TBP at water:hexane interface



Amphiphilic TBP

Microsolvation in Region (II) 10-20 Å





- Only TBP increases the microsolvation in the Region II.

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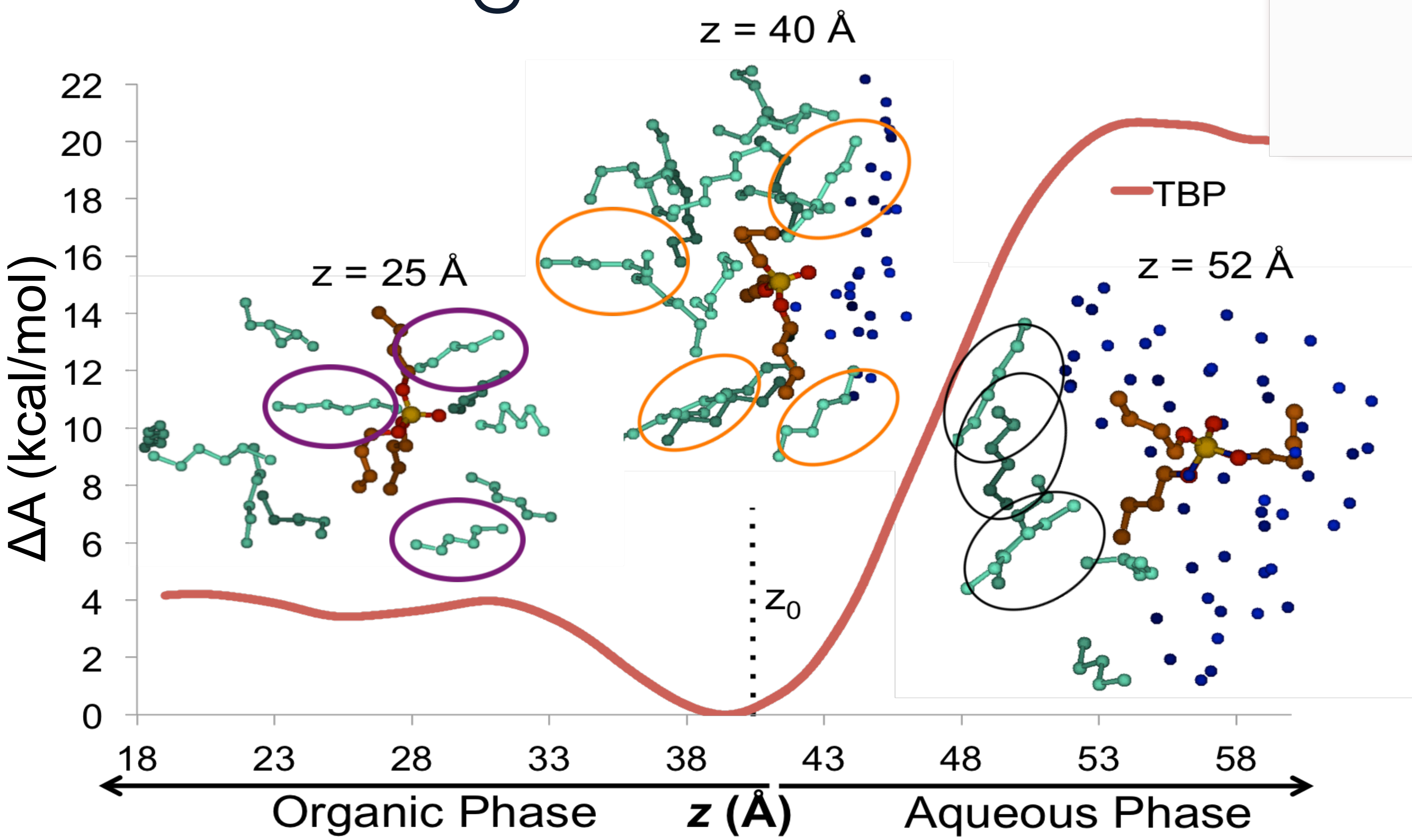
Configuration of TBP at Different Regions



- TBP adopts a "Y" shape configuration at the interface – alters hexane orientation.
- This leads to an increase in microsolvation

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Summary

- Bulk solution conditions alter interfacial properties
  - Aqueous ionic strength
  - Branching of akyl solvents
- Mutual miscibility of co-solvents measured by microsolvation reactions (concentration of co-solvent)
  - Is this related to permeability to solute transport? (examining correlations with PMF's now)
- Relationships between macroscopic interfacial properties and microsolvation is unclear
  - We need more data…want to systematically examine binary solutions from miscible to immiscible
  - Third-phase formation
- Solutes at interface can have an impact even at long-range
- Analyzing higher concentration TBP data now…role of aggregation is apparent

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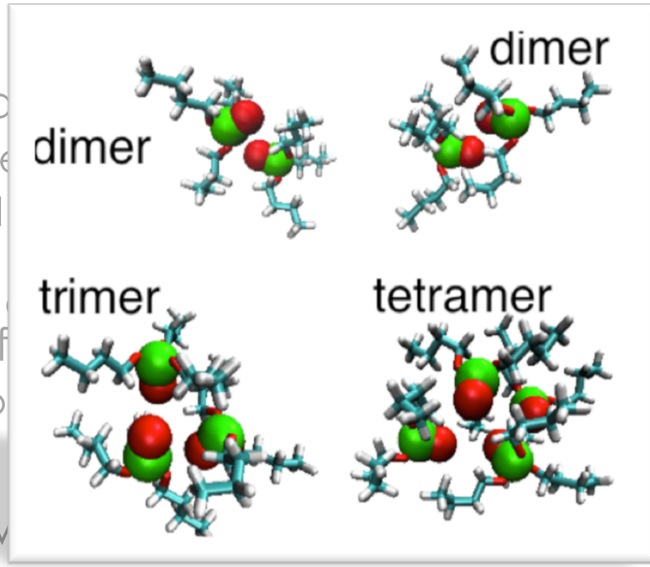

Servis, M. J.; Tormey, C. A.; Wu, D. T.; Braley, J. C. *J. Phys. Chem. B.* 2016, *ASAP article* DOI: 10.1021/acs.jpcb.5b08579

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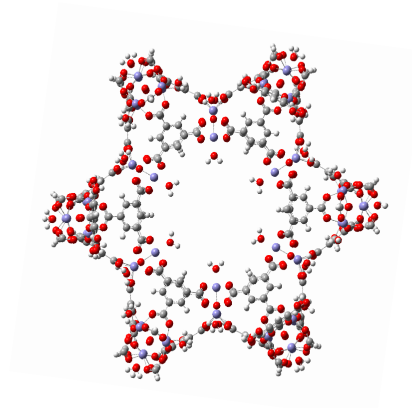
Related work performed at OLCF

- Materials for separation
  - Metal organic frameworks



    - Ligand binding is accompanied by affects of confinement upon the solvent
    - Synthesis of these materials is incredibly challenging
      - Hydrothermal synthesis where solution composition alters the topology

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Not Pictured: Yasi Ghadar, Morgan Kelley

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